USER MANUAL FOR RT1D – Multi-Component **R**eactive **T**ransport Model for **1-D** Systems

(RT1D–v1.0 Beta)

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RT1Dv1.0 (beta) is an EXCEL based VB code; this first beta version was coded by Dr. Torlapati as part of his PhD dissertation research completed at Auburn University. RT1D uses several numerical solvers and routines that were originally available within the FORTRAN tool RT3D and the associated research software tools. Therefore, we first like to thank the RT3D development team members who, over the past two decades, have contributed several ideas in this area while working with Professor Clement at Battelle Pacific Northwest National Laboratory and at University of Western Australia. We also like to thank the researchers at Auburn University who have developed various types of reactive transport models while working in Professor Clement's research group-- Dr. Tirtha Gautham, Anjani Kumar and Dr. Gautham Jeppu developed various types of geochemical reaction models and coupled them with transport routines; their FORTRAN models provided a template for developing the geochemistry module in RT1D. Jared McLaughlin investigated various types of TVD solvers during his tenure at Auburn University. We like to thank Dr. Charles E. Schaefer of Shaw Environmental and Infrastructure, NJ, for his support in developing some of the reaction packages discussed in this manual. This code development effort was, in part, funded by the Office of Science (BER), U.S. Department of Energy Grant No. DE-FG02-06ER64213, Auburn University.

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1. INTRODUCTION

Reactive transport problems in porous media systems could be mediated by either kinetic or equilibrium processes. Kinetic models are used to describe relatively slow chemical reactions, whereas equilibrium reactions are used to describe fast chemical reactions. Several reaction transport codes are available in the literature, but they can only handle kinetic type reactions (e.g., RT3D) or can handle equilibrium type reactions (Cederberg *et al.*, 1985; Parkhurst and Appelo, 1999). RT1D was designed to provide a unified platform for simulating transport problems involving both geochemical and kinetic reactions. However, it is important to note that the current version can either simulate a set of pure kinetic reactions or a set of pure geochemical reactions, but one cannot mix both types of reactions.

The capabilities of RT1D model, which are designated as "simulation options," are summarized in Figure 1. The model currently supports four different "simulation options" involving the use of two types of reaction modules: a kinetic module and an equilibrium module which can simulate kinetic and equilibrium reactions, respectively. There are four types of simulation options available within RT1D. The first simulation option can be used to solve batch kinetic problems. The second option can be used to solve one-dimensional reactive transport problems involving kinetic reactions. The third option can solve batch equilibrium problems. The fourth option can solve one-dimensional reactive transport problems involving geochemical equilibrium reactions. If the kinetic module is selected, the user should also provide a problem-dependent reaction package. The kinetic module supports several standard reaction models that are already coded within a set of pre-programmed reaction packages. In addition to these preprogrammed packages, RT1D also supports a user-defined reaction package via which the user can input any type of kinetics. The geochemical module, on the other hand, does not require a problem-dependent reaction package, and instead uses a MICROQL-based chemistry package to solve the equilibrium problem. The information required for formulating a specific geochemical problem are input using the standard tableau.

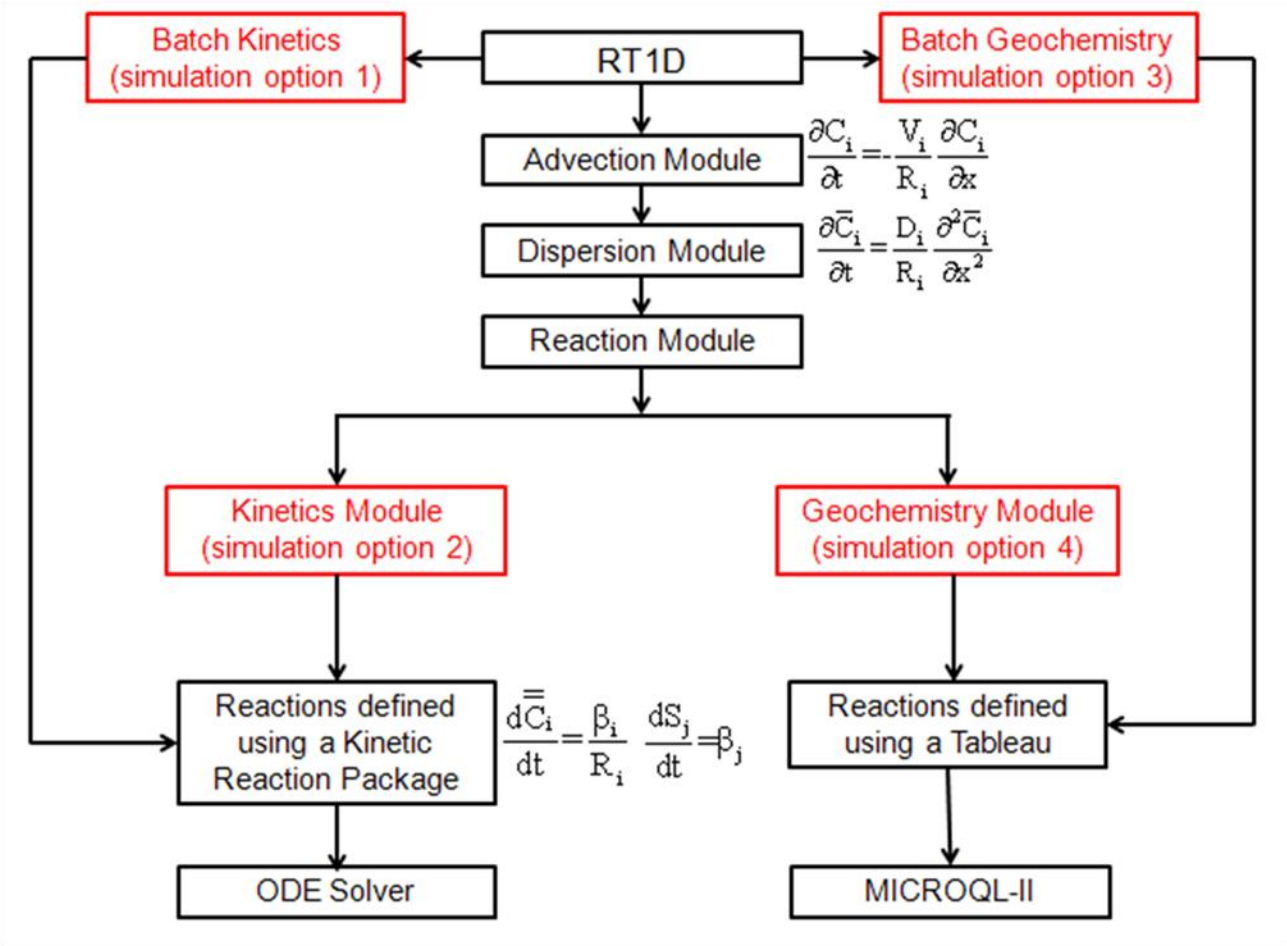


Figure 1. Simulation options available in RT1D

1.1 UNDERSTANDING THE SPREADSHEET

In this section, we will briefly discuss the different sections of the spreadsheet and illustrate their use to set up various types of batch or reactive transport problems. As explained in the earlier section, RT1D has four different simulation options. The data required for simulating these options are organized into three distinct sections within the input screen, as shown in Figure 2. The parameters for the transport module should be input in Section-1(see Figure 2). These parameters are used by the model when a simulation option involving transport is selected (2 or 4). The left side of Section-2 is used for defining kinetic-type problems, whereas the right side is used for the geochemistry equilibrium problems. Depending on the type of problem, only one of these two sections will be used. The program automatically sets the unused options to "N/A". The Section-3 in Figure 2 is a "Generate Input Template" button that will automatically generate a spreadsheet input table depending on the simulation option and the reaction-type parameters set in Section-2. It can be observed from this figure that the input for kinetic-type reaction has been set to "N/A" by the program after pressing the button in Section-3. An example for a kinetic-type input sheet is shown in Figure 4.

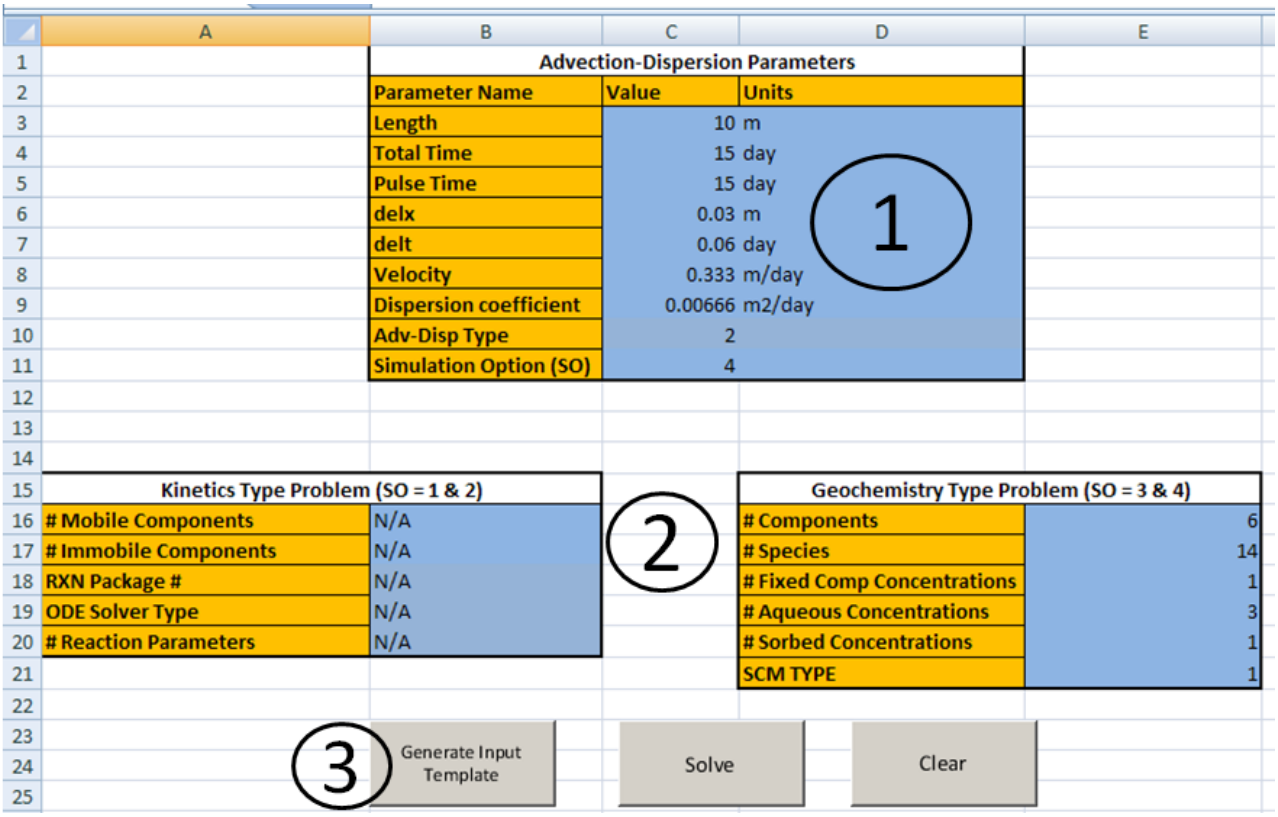


Figure 2. Spreadsheet layout for RT1D parameters to generate reaction-specific input template

In the following section, we will briefly discuss various steps involved in running a simulation using RT1D. The parameters and the required short codes for each module and options are made available in a textbox in the spreadsheet for the convenience of the user.

Step 1: Transport module - To perform simulations that involve the use of a transport module, the advection-dispersion parameters along with the length of the column need to be input in their respectively columns in Section-1. The total simulation time and the amount of time for which the concentration pulse has been input should also be provided by the user. For a continuous pulse, the pulse time should be equal to the total simulation time. The user should also provide the type of advection-dispersion solver to be used for the transport module. The simulation option (SO) describes the different types of problems that RT1D can solve. The options are: batch kinetics (1), kinetic-reaction coupled reactive transport (2), batch geochemistry (3), and geochemistry-coupled reactive transport (4)

Step 2: Simulation option parameters – Depending on the simulation option chosen within Section-1, the kinetic or the geochemistry parameters should be input in Section-2. For a kinetic-type problem, the user should input total number of mobile and immobile components, the reaction package number and type of ODE solver module used to solve the reaction package. The user can also set the total number of user-defined reaction parameters (kinetic parameters) that will be used within the reaction package.

For a geochemistry problem, the user should input the number of components, species, components whose concentrations are fixed (example: fixed pH), number of aqueous component concentrations that need to be tracked, number of sorbed concentrations that are required for correcting the aqueous concentrations during transport and the type of surface complexation model. This information is input in the form of standard reaction tableau (Westall, 1976).

Step 3: Generate the input template – The "Generate Input Template" button shown in Section-3 of Figure 2 will generate a table to enter the parameters specific to the kind of simulation option selected by the user. Example input template for a kinetic-type and geochemistry equilibrium-type problem are shown in Figures 3 and 4, respectively. The Section-4 shown in these figures changes depending on the parameters set in Section-2 of the spreadsheet.

For the simulation options 1 and 2 (kinetic), the button generates a template to input retardation factor, initial and boundary conditions based on the number of mobile and immobile species entered in Section-2. The input template also provides an area for the user to input reaction parameters specific to that reaction package.

For the simulation options 3 and 4 (geochemistry), the button (3) will generate an input layout similar to Figure 3 to enter the tableau, surface complexation parameters, initial and boundary conditions for the aqueous component concentrations, initial condition for the sorbed concentrations, the composition of the sorbed concentrations and the surface complexation parameters.

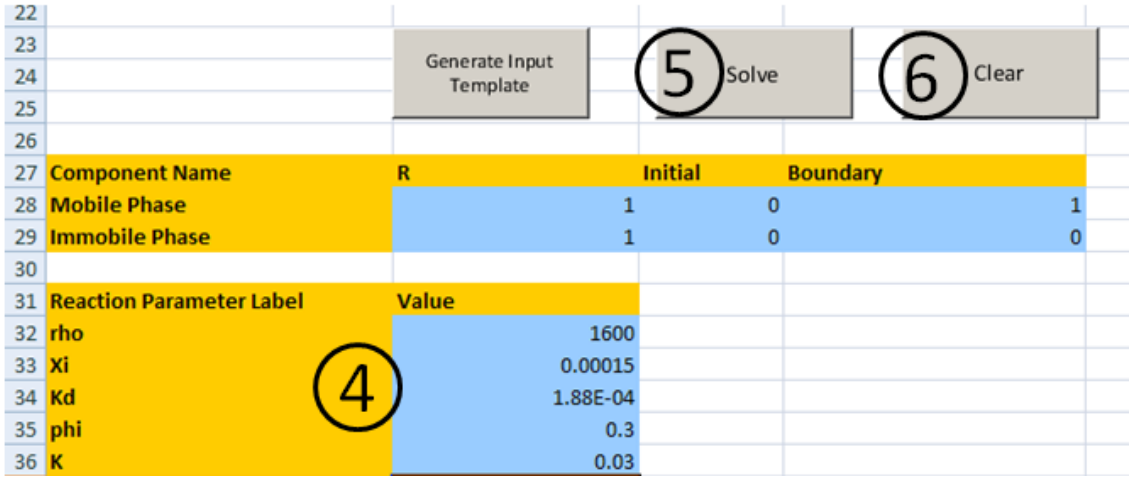


Figure 3. Example input template for a kinetic problem

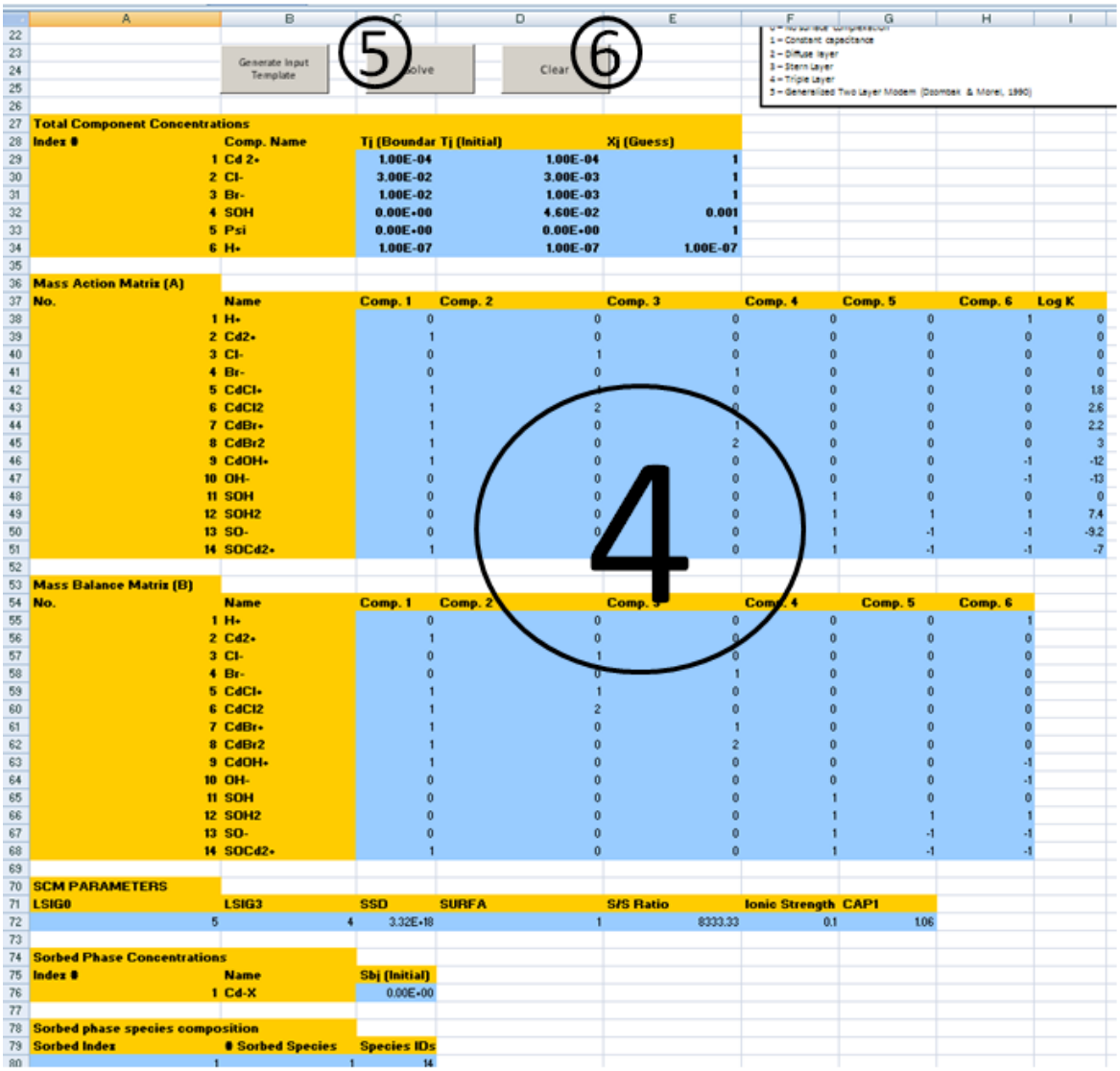

Generate Input Template
5
Solve
Clear
6
1 – Constant capacitance
2 – Diffuse layer
3 – Stern layer
4 – Triple layer
5 – Generalised Two Layer Modem (Dzombak & Morel, 1990)
Total Component Concentrations
Index #
Comp. Name
Tj (Boundar
Tj (Initial)
Xj (Guess)
1 Cd 2+ 1.00E-04 1.00E-04 1
2 Cl- 3.00E-02 3.00E-03 1
3 Br- 1.00E-02 1.00E-03 1
4 SOH 0.00E+00 4.60E-02 0.001
5 Psi 0.00E+00 0.00E+00 1
6 H+ 1.00E-07 1.00E-07 1.00E-07
Mass Action Matrix (A)
No.
Name
Comp. 1
Comp. 2
Comp. 3
Comp. 4
Comp. 5
Comp. 6
Log K
1 H+ 0 0 0 0 0 1 0
2 Cd2+ 1 0 0 0 0 0 0
3 Cl- 0 1 0 0 0 0 0
4 Br- 0 0 1 0 0 0 0
5 CdCl+ 1 1 0 0 0 0 1.8
6 CdCl2 1 2 0 0 0 0 2.6
7 CdBr+ 1 0 1 0 0 0 2.2
8 CdBr2 1 0 2 0 0 0 3
9 CdOH+ 1 0 0 0 0 -1 -12
10 OH- 0 0 0 0 0 -1 -13
11 SOH 0 0 0 1 0 0 0
12 SOH2 0 0 0 1 1 1 7.4
13 SO- 0 0 0 1 -1 -1 -9.2
14 SOCd2+ 1 0 0 1 -1 -1 -7
Mass Balance Matrix (B)
No.
Name
Comp. 1
Comp. 2
Comp. 3
Comp. 4
Comp. 5
Comp. 6
1 H+ 0 0 0 0 0 1
2 Cd2+ 1 0 0 0 0 0
3 Cl- 0 1 0 0 0 0
4 Br- 0 0 1 0 0 0
5 CdCl+ 1 1 0 0 0 0
6 CdCl2 1 2 0 0 0 0
7 CdBr+ 1 0 1 0 0 0
8 CdBr2 1 0 2 0 0 0
9 CdOH+ 1 0 0 0 0 -1
10 OH- 0 0 0 0 0 -1
11 SOH 0 0 0 1 0 0
12 SOH2 0 0 0 1 1 1
13 SO- 0 0 0 1 -1 -1
14 SOCd2+ 1 0 0 1 -1 -1
SCM PARAMETERS
LSIG0
LSIG3
SSD
SURFA
S/S Ratio
Ionic Strength
CAPI
5 4 3.32E+18 1 8333.33 0.1 1.06
Sorbed Phase Concentrations
Index #
Name
Sbj (Initial)
1 Cd-X 0.00E+00
Sorbed phase species composition
Sorbed Index
Sorbed Species
Species IDs
1 1 14
4

Figure 4. Example input template for a geochemical equilibrium problem

Step 4: Solve – Prior to running a simulation, the user should ensure that the following list of tasks are completed:

a) **Kinetic problem - Simulation options (1 & 2)**
   i. Select an existing reaction package from the several built-in packages using the short code.
   ii. Program your own kinetic reaction package by opening the code editor.
   iii. Input the reaction parameters as necessary.
   iv. Click the solve button shown in Section-5 to perform the simulation

b) **Geochemistry equilibrium problem – Simulation options (3 & 4)**
   i. Input the total component concentrations at the boundary and the initial concentrations at the nodes, if any.
   ii. Input the guess concentrations, this is used by the solver for the starting solution to converge to the correct solution. A good starting point would be the total concentration. Please do not input "0" for the guess values as the logarithm is calculated for these guess concentrations as a part of the solution process.
   iii. Input the tableau and the surface complexation parameters, if any.
   iv. Input the initial sorbed concentration present in the column and the species that combine to form the sorbed concentration. This sorbed concentration is used to calculate the aqueous species concentrations at each time step.
   v. Click the solve button shown in Section-5 to perform the simulation

Step 5: Viewing the solutions: The results are presented in Sheets 2 & 3 of the model spreadsheet. Sheet 2 provides the spatial variation of the component concentrations after the completion of the simulation time. Sheet 3 provides the breakthrough component concentrations at the outlet after each time step. By default, the breakthrough component concentrations are printed at the last node (end of the column). The program can be modified to print the breakthrough component concentrations at any node in the column.

WARNING!! - The spreadsheet erases the data below the buttons (after cells A27) when either button 3 or 6 are pressed. The output data in Sheets 2 & 3 is cleared every time the button 5 is pressed. The user is advised to use a different a spreadsheet for post-processing the results, and for completing other intermediate calculations.

1.2 INPUT SPREADSHEET LABEL DETAILS

1.2.1 TRANSPORT MODULE

i. Length (L) – Length of the column for the transport module
ii. Total time (T) – Total simulation time

iii. Pulse time (T) – Total time for which the concentration is pumped through the column during the experiment at the boundary. This is less than or equal to the Total time set in (ii).

iv. delx (L) – Grid size. This is used to calculate the total number of nodes using the formula (length/delx)+1.

v. delt (T) – Time step. The total number of iterations is calculated using the formula (total time/delt).

vi. Velocity (LT^{-1}) – This is the pore velocity of the liquid flowing through the column. This is calculated from the flowrate (Q) as follows (Q/cross-sectional area)/porosity. Please make sure that units are same as the length/total time

vii. Dispersion coefficient (LT^{-2}) – This is the hydrodynamic dispersion coefficient calculated by multiplying the value of dispersivity with the velocity. Please provide the hydrodynamic dispersion coefficient value and not the dispersivity value. The code does not multiply with the velocity.

viii. Adv-Disp type – This takes a short code for the type of Advection-Dispersion solver. The choices are 0, 1, and 2 for explicit advection method, fully implicit advection-dispersion or TVD advection respectively. For choices 0 and 2, dispersion is solved by fully implicit dispersion module.

ix. Simulation option – Type of problem

1 - Batch Kinetics
2 - Reactive Transport
3 - Batch Geochemistry
4 - Geochemistry coupled with Transport

1.2.2 KINETIC REACTION MODULE

i. # Mobile components – This is the number of aqueous components inside the system. The mobile components will have an advection/dispersion and reaction term. There should be at least 1 mobile species for the program to work.

ii. # Immobile components – This is the number of solid phase components in the system that do not undergo advection-dispersion. They only undergo reaction. The immobile components will be placed at the bottom after all the mobile components. In the reaction package, the immobile species number will start after the mobile species. That is, if there are 6 mobile species and 2 immobile species, we will count the immobile species as 7 & 8. Please look at the example problem for further explanation.

iii. Reaction package # – This is a short code for the type of reaction kinetics. The different kinds of reaction kinetics that have been pre-programmed into the RT1D model. We will be adding more packages as we continue developing the model. The users can program their reaction kinetics by selecting Option 10.

1 – First order sequential degradation
2 – Four-component coupled sequential degradation (Quezada *et al.*, 2004)

3 – Four-component decay chain (Bauer *et al.*, 2001)
4 – Modified Monod kinetics of TCE bioaugmentation
5 – Rate-limited sorption (Benchmark problem – 1, Torlapati and Clement (2012))
6 – Denitrification (Benchmark problem – 2, Torlapati and Clement (2012))
7 – Biodegradation of Carbon Tetrachloride (Benchmark problem – 3, (Torlapati and Clement, 2012))
8 – Open
9 – Open
10 – User-defined reaction package

iv. ODE Solver type – Short code for the type of reaction solver
    0 – Adaptive Runge-Kutta-Fehlberg solver
    1 – Fourth order Runge-Kutta solver
v. # Reaction parameters – Set the number of user-defined reaction terms needed

1.2.3 GEOCHEMISTRY EQUILIBRIUM MODULE

These variables become active only when you're using the geochemistry module of the code. This is when you enter either 3 or 4 for the reaction type

i. # Components – Number of components
ii. # Species – Number of species
iii. # Fixed component concentrations – set the number of components whose concentrations are fixed (Example: fixed pH)
iv. # Aqueous components – number of aqueous components that we are tracking
v. # Sorbed concentrations – the number of solid phase concentrations that are necessary for correcting the aqueous phase component concentrations
vi. SCM TYPE – Type of surface complexation method.
    0 – No surface complexation
    1 – Constant capacitance
    2 – Diffuse layer
    3 – Stern Layer
    4 – Triple Layer
    5 – Generalized Two Layer Modem (Dzombak and Morel, 1990)

1.2.4 KINETIC REACTION PARAMETERS

These labels are generated in the Section-4 of Figure 3 when either simulation option 1 or 2 are selected. The spreadsheet displays four different columns requiring the input for the following parameters:

i. Component name: The input template automatically populates it with a default component name. This can be changed to a more appropriate name by the user. The program reads this name and uses for output in Sheets 2 and 3.

ii. R (Retardation factor): In case of linear sorption, we have a retardation factor. This retardation factor is given by $\left(1+\frac{\rho K_d}{\varphi}\right)$ where ρ is bulk density of the soil (mg/L), K_d is the linear sorption constant (L/mg) and φ is the porosity. This is equal to 1 when there is no sorption. Cannot be less than 1.

iii. Initial: This is the initial concentration of the species in the column. It is possible that there is a residual component concentration present in the column before the simulation time has begun. This option sets a constant initial concentration, as specified in the spreadsheet, across the all the nodes in the column. It is possible to set a variable initial concentration by modifying the *setinit()* subroutine in the code.

iv. Boundary: This is the inlet concentration of the species at time = 0. This boundary concentration will be supplied to the column until the end of the pulse time.

v. Reaction terms: Generates a table for entering the reaction terms and labels based on the total reaction terms.

1.2.5 GEOCHEMISTRY EQUILIBRIUM PARAMETERS (WITHOUT TRANSPORT)

The inputs are different when the geochemistry package is used with advection or without advection. The input template also changes based on the type of surface complexation reaction chosen in the geochemistry input sheet.

i. Mobile species: This presents with 4 columns of different parameters for the mobile species.
   a. Index # is the serial number of the component name. This is automatically populated and should not be changed
   b. Comp. Name: A default component name is generated automatically. It is advised that this component name be changed to something more suitable. The components with fixed concentration are input after all the variable components have been entered into the spreadsheet cells.
   c. Total concentration: If the total concentration of the component is known, please enter the value here.
   d. Guess concentration: If the values are unknown, please enter a guess value so the program has a starting value for the iteration process. The iterative process converges faster if suitable starting concentrations are chosen. A good guess for the guess concentration is the initial concentration itself unless it is zero. Since the logarithm of the guess concentrations are calculated during the solution procedure, please do not use 0's as guess concentrations. If the solution does not converge, try a different guess value or check the problem inputs.

ii. Tableau: This is the tableau where you fill in the stoichiometric matrix. Make sure the components are in the same order as the Total concentrations in the column. Also enter the Log K values in the end for each species for the mass action matrix.

iii. Additional parameters are required based on the surface complexation model chosen.
   a. LSIG0: Index for PSI0 in the component list [L0 in Westall (1979a)]
   b. LSIG1: Index for PSI1 in the component list [L1 in Westall (1979a)]
   c. LSIG2: Index for PSI2 in the component list [L2 in Westall (1979a)]

d. LSIG3: Index for SOH in the component list [L3 in Westall (1979a)]
e. SSD: Surface site density (sites/m^2) [C1 in Westall (1979a)]
f. SURFA: Specific surface area (m^2/g) [C2 in Westall (1979a)]
g. CONCS: Concentration of sorbing solid (g/L) [C3 in Westall (1979a)]
h. XMU: Ionic strength (moles/L) [C4 in Westall (1979a)]
i. CAP1: Inner capacitance (F/m^2) [C5 in Westall (1979a)]
j. CAP2: Outer Capacitance (F/m^2) [C6 in Westall (1979a)]

iv. Sorbed Species ID: When generating isotherms, the program requires Species index numbers of the sorbed species in the tableau. The number of sorbed species displayed here is based on the "Sorbed concentrations" set before pressing the "Generate Input Template" button. Please input all the ID's of the sorbed species here. This is used to calculate the amount of total sorbed species in moles/L. The program reads the concentrations of all the sorbed species entered here and displays the total sum of their concentrations as total sorbed concentration. In case of a speciation problem where the sorbed concentrations are not required, this should be left blank.

v. Component # of the aqueous species: This is only required when generating isotherms. Enter the component number of the aqueous species. The aqueous concentration of the component is calculated at the end of the simulation by subtracting the sorbed concentration from the total concentration of the component in moles/L.

1.2.6 GEOCHEMISTRY EQUILIBRIUM PARAMETERS (WITH TRANSPORT)

The input template is similar to the above except we need a few additional parameters. This section discusses only the additional parameters to avoid any repetition.

i. Boundary: The total concentrations of all the components at the inlet have to be entered here. The initial guess value for the concentrations is also entered here.

ii. Initial: The total residual concentration of the existing in the column before the beginning of the simulation.

iii. The tableau information is similar to the batch geochemistry problem

iv. Sorbed phase concentrations: The initial concentration of the sorbed species is input in the cells. The number of sorbed concentrations is dependent on the input parameter set in Section-2**.** The user needs to enter the sorbed species index and the initial concentration for the sorbed phase.

v. Sorbed phase species composition: In this section, we define the composition of sorbed phase concentrations. We have to provide the index of the sorbed phase concentration, and the number of species it is composed of and the species index # of all the species in the same row.

2. MODEL DETAILS AND NUMERICAL SOLUTION

The multi-component one-dimensional reactive transport model developed in this study, designated as RT1D, solves a coupled set of advection-dispersion-reaction equations for a total of "n" components. The model simulates the transport of "m" mobile components that are either fully or partially coupled to a set of "n-m" immobile components. The reactions between these components could be mediated by biological/geochemical kinetic reactions, or geochemical equilibrium reactions. The governing set of equations solved by the model can be written in a general form:

$$\frac{\partial C_i}{\partial t} = -\frac{V}{R_i}\frac{\partial C_i}{\partial x} + \frac{D}{R_i}\frac{\partial^2 C_i}{\partial x^2} + \frac{\beta_i}{R_i} \quad \text{where } i = 1, 2, 3 \ldots m \tag{1}$$

$$\frac{\partial S_j}{\partial t} = \beta_j \quad \text{where } j = (m+1), (m+2), (m+3), \ldots (n) \tag{2}$$

where V is the velocity (m/day); D is the hydrodynamic dispersion coefficient (m^2/day), C_i is the aqueous phase concentration (mg/L) of a mobile component i; S_j is the solid phase concentration (mg/mg) of an immobile component j; m is the total number of mobile components; n is the total number of components (note that a total of (n-m) immobile components are numbered sequentially after numbering all the mobile components); R_i is the linear retardation factor of the i^{th} mobile component [$R = \left(1 + \frac{\rho K_d}{\varphi}\right)$, where ρ is the bulk density (mg/L); φ is the porosity; K_d is the linear sorption constant (L/mg)]; and β_i and β_j are the reactions involving mobile and immobile components, respectively. The expressions used for β_i and β_j terms would vary depending on the type of reactions involved in the system. Note the immobile component equations do not have advection dispersion terms, but will have reaction terms that will be coupled to some of the mobile component reaction terms. Also, the mobile-component reaction terms themselves could be coupled to each other.

The coupled set of reactive transport equations, represented by equations (1) and (2) are solved using the operator split approach (Clement *et al.*, 1998; Torlapati and Clement, 2012). Using this approach, the governing set of transport equations can be written as:

$$\frac{\partial C_i}{\partial t} = -\frac{V}{R_i}\frac{\partial C_i}{\partial x} \tag{3}$$

$$\frac{\partial \overline{C_i}}{\partial t} = \frac{D}{R_i}\frac{\partial^2 \overline{C_i}}{\partial x^2} \tag{4}$$

$$\frac{d\overline{\overline{C_i}}}{dt} = \frac{\beta_i}{R_i} \tag{5}$$

$$\frac{dS_j}{dt} = \beta_j \tag{6}$$

In the numerical code, the advection terms in all the mobile components (equation 3) are first solved using an advection solver module. Next, the advected concentrations ($\bar{C}$) are used to solve for dispersion terms (equation 4) in the mobile component transport equations using a dispersion solver module. Finally, the dispersed concentrations ($\bar{\bar{C}}$) are used to solve a set of coupled reaction terms involving both mobile and immobile components, represented by equations (5) and (6). For transport problems involving kinetic reactions, the reaction part of the transport equations (equations 5 & 6) would yield a set of coupled ODEs. These ODEs, referred as the kinetic reaction package, are solved using an ODE solver. For transport problems involving geochemical equilibrium reactions, the reaction terms would yield a set of coupled non-linear equations. These non-linear equilibrium equations are represented using the tableau approach (Westall, 1976) and are solved using the geochemical equilibrium solver, MICROQL, developed by (Westall, 1979a, b).

2.1 TRANSPORT MODULE

The advection module provides two explicit solver options: a total variation diminishing (TVD) solver and an explicit finite difference solver that uses backward difference approximation. The advected concentrations are then used to solve the dispersion equation, within the dispersion module, using the implicit finite difference method. In addition to these explicit-implicit solvers, there is also a fully-implicit option that solves the advection-dispersion terms together using a fully-implicit approach.

2.1.1 EXPLICIT ADVECTION SCHEME

The advection part of the transport equation can be solved using the explicit backward difference approximation as shown below:

$$\left(\frac{C_i^{n+1} - C_i^n}{\Delta t}\right) = -\frac{V}{R_i}\left(\frac{C_i^n - C_{i-1}^n}{\Delta x}\right) \tag{7}$$

where C_i^{n+1} is the concentration of the component at the current time step at the current node; C_i^n is the concentration of the mobile component at the previous time step at the current node and C_{i-1}^n is the concentration of the mobile component at the previous time step at the preceding node. After further simplification, we can solve for the concentration of mobile component at the current node (C_i^{n+1}) as shown below:

$$C_i^{n+1} = -\frac{Cr}{R_i}\left(C_i^n - C_{i-1}^n\right) + C_i^n \tag{8}$$

where $Cr = \left(\frac{V\Delta t}{\Delta x}\right)$ is known as the grid Courant number.

2.1.2 EXPLICIT TVD SCHEME

Numerical dispersion is a major concern while solving the advection dominated problems. RT1D includes a robust total variation diminishing (TVD) scheme that minimizes numerical dispersion errors. Details of this scheme are given below. Using the Taylor series expansion, the standard Lax-Wendroff (LW) scheme for the advection term can be written as (Leveque, 2002):

$$C_i^{n+1} = C_i^n - \frac{Cr}{2}(C_{i+1}^n - C_{i-1}^n) + \frac{Cr^2}{2}(C_{i+1}^n - 2C_i^n + C_{i-1}^n) \tag{9}$$

The above equation can be rearranged and written in a flux-balance format as:

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = -\frac{F_{i+1/2}^n - F_{i-1/2}^n}{\Delta x} \tag{10}$$

Where $F_{i+1/2}^n = VC_i^n + \frac{V}{2}(1-Cr)(C_{i+1}^n - C_i^n)$ and $F_{i-1/2}^n = VC_{i-1}^n + \frac{V}{2}(1-Cr)(C_i^n - C_{i-1}^n)$ respectively. Note the flux terms defined above consist of a lower and higher order flux terms. The lower order flux term in $F_{i+1/2}^n$ is VpC_i and the higher order term in $F_{i+1/2}^n$ is $\frac{V}{2}(1-Cr)(pC_{i+1} - pC_i)$.

Furthermore in TVD schemes, a flux limiter will be used to minimize the potential numerical oscillations induced by the higher order term as shown below:

$$F_{i+1/2}^n = VC_i^n + \frac{V}{2}(1-Cr)(C_{i+1}^n - C_i^n) * \Phi \tag{11}$$

Different types of flux limiters are available in the literature and in this study we have used the Van-leer flux limiter given as (Leveque, 2002):

$$\Phi = \frac{\theta + |\theta|}{1 + |\theta|} \tag{12}$$

Where $\theta = \frac{C_i^n - C_{i-1}^n}{C_{i-1}^n - C_{i-2}^n}$

2.1.3 IMPLICIT FINITE DIFFERENCE METHOD FOR DISPERSION SCHEME

The dispersion part of the transport equation can be numerically discretized using a central difference approximation.

$$R_i \frac{\overline{C_i^{n+1}} - \overline{C_i^n}}{\Delta t} = D \frac{\overline{C_{i-1}^{n+1}} - 2\overline{C_i^{n+1}} + \overline{C_{i+1}^{n+1}}}{\Delta x^2} \tag{13}$$

Where C_{i-1} is the concentration at the previous node for the current time step, C_{i+1} is the concentration at the next node for the current time step. The above equation can be further simplified as follows

$$-\overline{C_i^n} = \frac{\lambda}{R_i}\overline{C_{i-1}^{n+1}} + \overline{C_i^{n+1}}\left(-\frac{2\lambda}{R_i} - 1\right) + \frac{\lambda}{R_i}\overline{C_{i+1}^{n+1}} \tag{14}$$

Where $\lambda = \frac{D\Delta t}{\Delta x^2}$. Assembling equation (14) on a node-by-node basis would yield a following tri-diagonal matrix of the form:

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ a & b & c & 0 & 0 & 0 & 0 \\ 0 & a & b & c & 0 & 0 & 0 \\ 0 & 0 & a & b & c & 0 & 0 \\ 0 & 0 & 0 & a & b & c & 0 \\ .. & .. & .. & .. & .. & .. & . \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \overline{C}_1^{n+1} \\ \overline{C}_2^{n+1} \\ \overline{C}_3^{n+1} \\ \overline{C}_4^{n+1} \\ \overline{C}_5^{n+1} \\ .. \\ \overline{C}_n^{n+1} \end{bmatrix} = \begin{bmatrix} C_0 \\ d_2 \\ d_3 \\ d_4 \\ d_5 \\ .. \\ d_n \end{bmatrix} \tag{15}$$

Where $a = \frac{\lambda}{R_i}$, $b = \left(-\frac{2\lambda}{R_i} - 1\right)$, $c = \frac{\lambda}{R_i}$ and $d = -\overline{C}_i^n$; C_o is the concentration at the boundary node. The above matrix can be solved using a tridiagonal matrix solver to solve for all the unknown concentrations at the new time level.

2.1.4 FULLY IMPLICIT NUMERICAL SOLUTION FOR ADVECTION-DISPERSION

In this option, we solve the advection and dispersion together implicitly. We use a central difference approximation for the advection term and the numerically discretized form for the advection-dispersion equation is as follows:

$$\left(\frac{C_i^{n+1} - C_i^n}{\Delta t}\right) = -\frac{V}{R_i}\left(\frac{C_{i+1}^{n+1} - C_{i-1}^{n+1}}{2\Delta x}\right) + \frac{D}{R_i}\left(\frac{C_{i-1}^{n+1} - 2C_i^{n+1} + C_{i+1}^{n+1}}{\Delta x^2}\right) \tag{16}$$

The above equation can be further simplified as follows:

$$-C_i^n(R_i.\Psi)=(\alpha+1)C_{i-1}^{n+1}+(-2-R_i.\Psi)C_i^{n+1}+(1-\alpha)C_{i+1}^{n+1} \quad (17)$$

where $\Psi=\left(\frac{\Delta x^2}{D\Delta t}\right)$ and $\alpha=\frac{V\Delta x}{2D}$.

Expanding the equation (17) for all the nodes would yield a tridiagonal matrix similar to 15. For this problem, the values of a, b, c and d are given as $\alpha+1$, $2-R_i.\Psi$, $1-\alpha$ and $-C_i^n(R_i.\Psi)$, respectively.

2.2 REACTION MODULE

2.2.1 KINETIC TYPE PROBLEM

For a multi-species, the reaction part shown in equation (5) & (6) simplifies into a set of ordinary differential equations (ODE). These ODEs are referred to as a reaction package. The set of ODEs described within a kinetic reaction package can be solved using two different ODE solvers: a standard 4th order Runge-Kutta (RK) solver, or a more robust Runge-Kutta-Fehlberg (RKF) solver (Chapra and Canale, 1998). The RK solver uses a constant reaction time step, whereas the RKF solver will automatically subdivide the reaction time step into sub steps to minimize the local error.

2.2.2 GEOCHEMISTRY EQUILIBRIUM TYPE PROBLEM

The geochemical equilibrium reaction problem is formulated in the form of a tableau that represents the interactions between all the components and species involved in the chemical system. As defined by Westall (1976), a species is a chemical entity of interest present in the system whereas a component is a basic building block used for forming various chemical species in the system. The stoichiometric relationship between the components and the species can be represented in the form of a matrix known as the tableau. The chemical speciation problem, defined by the tableau, is solved using an EXCEL-VBA version of MICROQL code. The details of the numerical solution schemes employed by MICROQL are discussed in Westall (1979b). Within RT1D, the transport equations that involve geochemical (or equilibrium) reactions are solved using an approach proposed by Cederberg *et al.* (1985), which is slightly different from the approach used for the solving the transport equations involving kinetic reactions. As discussed in Cederberg *et al.* (1985), first the aqueous concentration of a component of interest will be transported using the transport module. The aqueous concentration of a component at a particular node is calculated by subtracting the concentrations of all the sorbed species associated with that component from its total concentration. After the transport step, the updated (advection-dispersed) aqueous component concentration is added back to the sorbed concentrations of the respective component to compute the total component concentration at that

node. This total component concentration is then transferred to MICROQL to solve the geochemical speciation problem. The equilibrated species concentrations are used to update the values of aqueous component concentrations for the next time transport step. Further details of this transport algorithm are discussed in Cederberg *et al.* (1985).

3. PROGRAM DETAILS
3.1 LIST OF SUBROUTINES

i. An input generator based on the number of species and the type of reaction
    a. Subroutine to generate input template for kinetic transport & batch reactions
    b. Subroutine to generate input template for the geochemical equilibrium problems
    c. Subroutine to generate input template for the geochemical equilibrium problems coupled with transport.
ii. RT1D_Main program that calls the required subroutines based on the advection solver and reaction type
iii. Subroutine to set the boundary condition based on the pulse time
iv. Subroutine to set the initial condition
v. The backward difference explicit advection solver
vi. TVD solver with van-leer flux limiter for advection
vii. Implicit finite difference solver for dispersion
viii. Fully-implicit finite difference solver for advection-dispersion
ix. Tridiagonal solver for solving the tridiagonal matrix generated by the implicit finite difference method for dispersion
x. Fourth order Runge-Kutta solver for solving ODEs in reaction package
xi. Adaptive Runge-Kutta-Fehlberg solver for solving ODE's in the reaction package
xii. MICROQL II with surface complexation reactions for geochemistry package
xiii. Subroutine to couple the advection solvers with MICROQL package.

3.2 TRANSPORT MODULES

The explicit finite difference schemes used in the advection modules of RT1D program are constrained by certain stability condition criteria. To ensure that the results generated by the numerical models are stable and error-free, researchers have used Courant number (Vdx/(R.dt)) and Peclet number (Vdx/D) to determine the grid size and time step for the simulations. In the following sections, we have tested the stability of our numerical models for different Courant and Peclet numbers. For explicit schemes, the Courant number should be less than 1 to obtain oscillation free results. If the Courant number exceeds 1, numerical oscillations are observed near the advective front. In addition, to obtain good quality solution the Peclet number should be set below 2.

3.2.1 PURE ADVECTION

In this section, we tested the Explicit and TVD schemes for different Courant numbers by setting the value of dispersion to 0. Simulations were performed for a one-dimensional column of 50 cm length. The pore velocity was about 1 cm/day and the simulations were performed for duration of 20 days. The grid size was set to 1 cm and the time step was varied to generate Courant numbers of 1, 0.5, 0.1 and 0.01. A constant boundary condition of 1 mg/L was supplied at the inlet for the

complete duration of the experiment. The results of the simulations for the Explicit and TVD schemes are shown in Figure 5 and 6 respectively. It can be observed from these figures that at Courant number 1, the results from both the advection schemes produce sharp advective fronts. However, the numerical dispersion comes into effect as the Courant number is decreased. The numerical dispersion is comparatively less in case of TVD schemes than the explicit schemes.

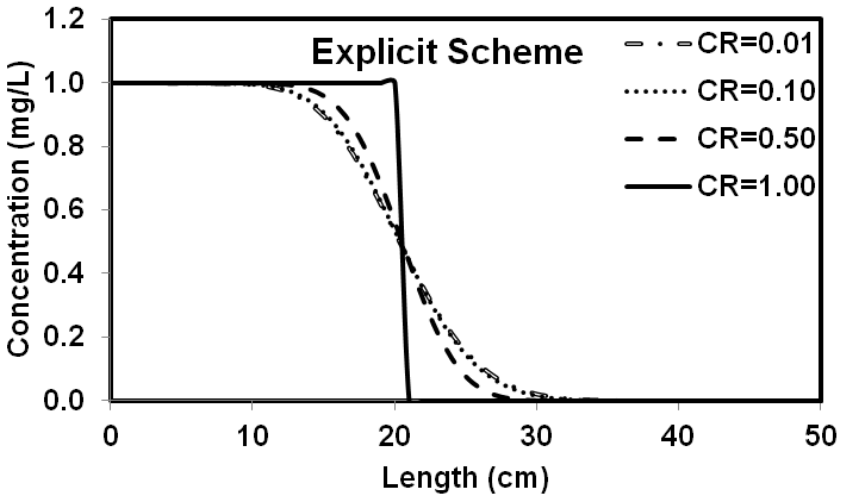


Figure 5. RT1D results for different Courant numbers for the explicit advection scheme with v=1 cm/day, dx=1 and a duration of 20 days

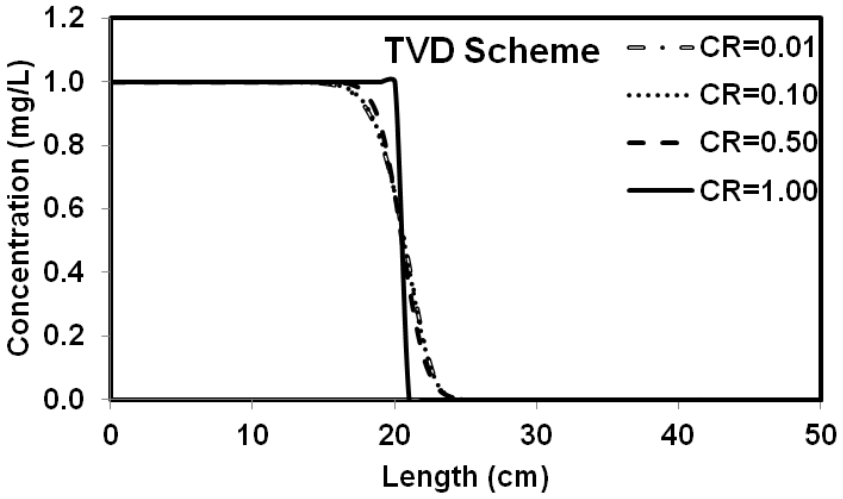


Figure 6. RT1D results for different Courant numbers for the TVD advection scheme with v=1 cm/day, dx=1 and a duration of 20 days

3.2.2 ADVECTION DISPERSION MODULES

The program was tested for a high and low Peclet numbers of 0.5 and 2 respectively for varying Courant numbers 0.01, 0.1, 0.5 and 1. A hydrodynamic dispersion coefficient of 0.05 cm^2/day was used to perform high Peclet number simulations and a hydrodynamic dispersion coefficient of 0.2 cm^2/day was used to perform low Peclet number simulations. A grid size of 0.1 cm and a pore velocity of 1 cm/day were used to perform the simulations. The results from these simulations were compared against the analytical solutions presented in van Genuchten and Alves (1982).

3.2.2.1 EXPLICIT ADVECTION AND IMPLICIT DISPERSION

Simulations were performed with a time step of 0.1, 0.05, 0.01 and 0.001 for both high and low Peclet numbers to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 7 and 8 show the results for low and high Peclet number simulations respectively.

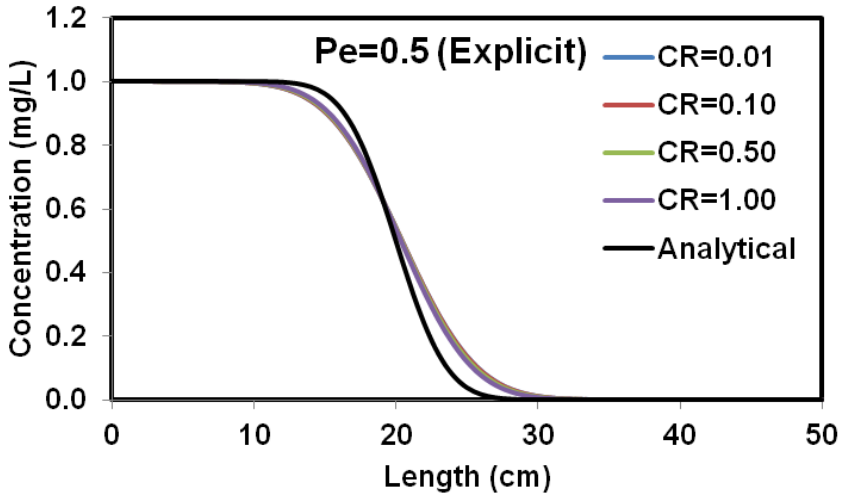


Figure 7. RT1D results for low Peclet number simulations with varying Courant number using the explicit advection and implicit dispersion scheme (v=1cm/day, D=0.2 cm^2/day, dx=0.1cm)

It was observed from the figures that the explicit scheme showed numerical dispersion in the presence of low Peclet number and this numerical dispersion decreased with increase in the Peclet number and the simulation results were closer to the analytical solutions.

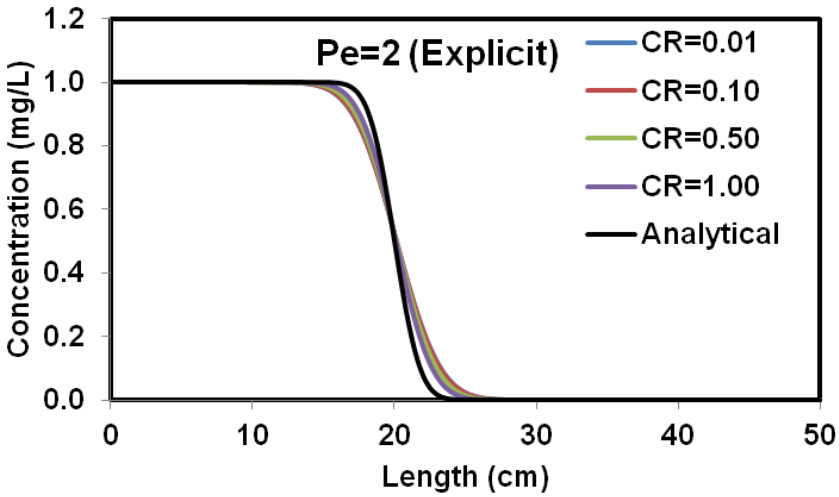


Figure 8. RT1D results for high Peclet number simulations with varying Courant number using the Explicit advection and Implicit dispersion scheme (v=1cm/day, D=0.05 cm^2/day, dx=0.1cm)

3.2.2.2 FULLY IMPLICIT ADVECTION DISPERSION SCHEME

Simulations were performed with a time step of 0.1, 0.05, 0.01 and 0.001 for both high and low Peclet numbers using the fully implicit advection dispersion scheme to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 9 and 10 show the results for low and high Peclet number simulations respectively.

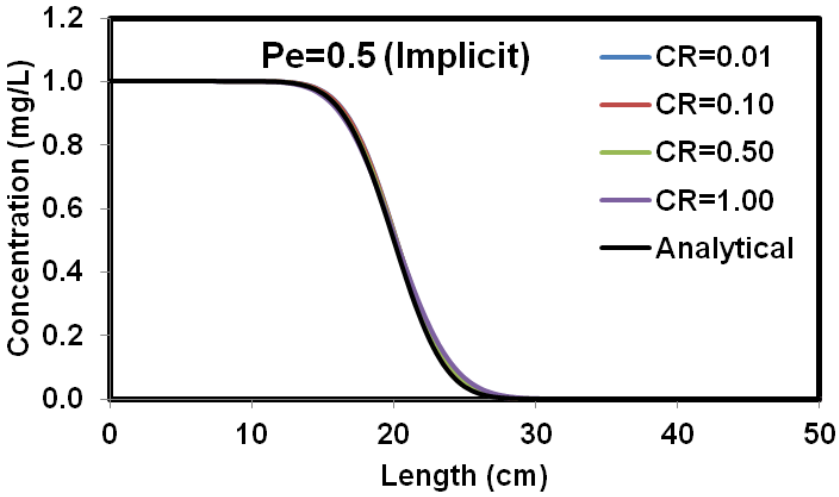


Figure 9. RT1D results for low Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=1cm/day, D=0.2 cm^2/day, dx=0.1cm)

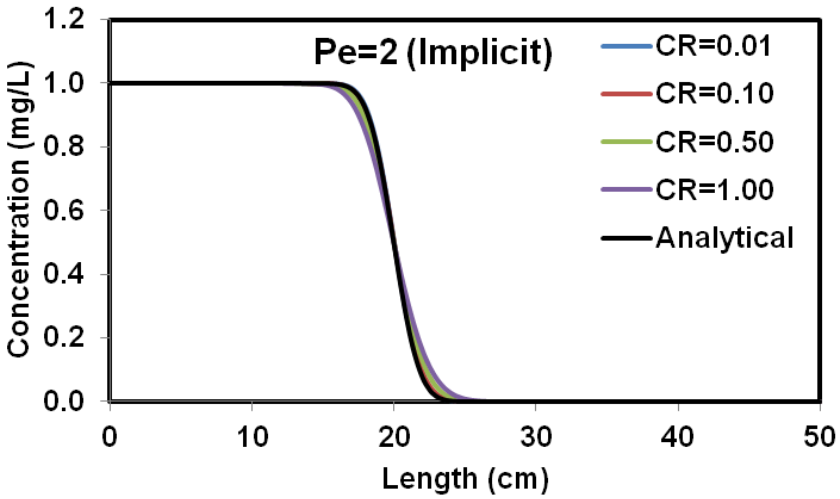


Figure 10. RT1D results for high Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=1cm/day, D=0.05 cm^2/day, dx=0.1cm)

It was observed from the simulations that the fully implicit scheme performed a lot better than the explicit scheme. However there was some numerical dispersion when the Peclet number was high.

3.2.2.3 TVD ADVECTION AND IMPLICIT DISPERSION SCHEME

Simulations were performed with a time step of 0.1, 0.05, 0.01 and 0.001 for both high and low Peclet numbers using the TVD advection and implicit dispersion scheme to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 11 and 12 show the results for low and high Peclet number simulations respectively. It was observed from the results that the TVD scheme was consistent with the analytical results for all the Courant and Peclet numbers. It is highly recommended that the users of the RT1D use TVD scheme for accurate results.

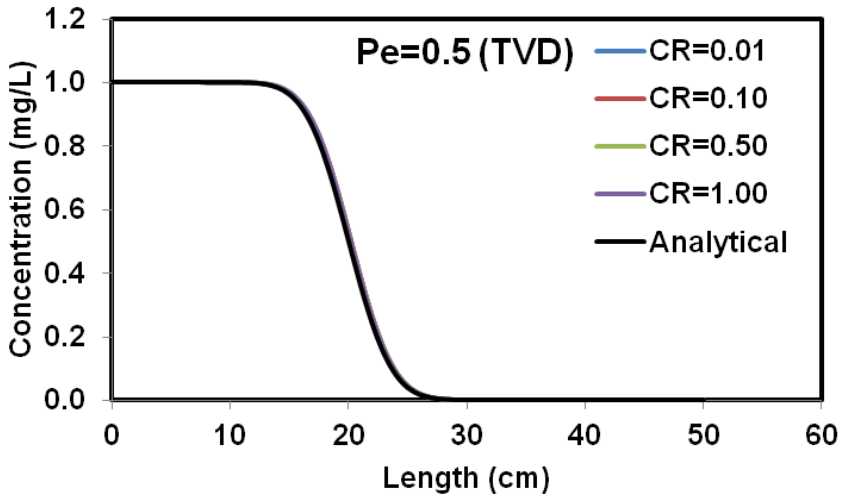


Figure 11. RT1D results for low Peclet number simulations with varying Courant number using the TVD advection and implict dispersion scheme (v=1cm/day, D=0.2 cm^2/day, dx=0.1cm)

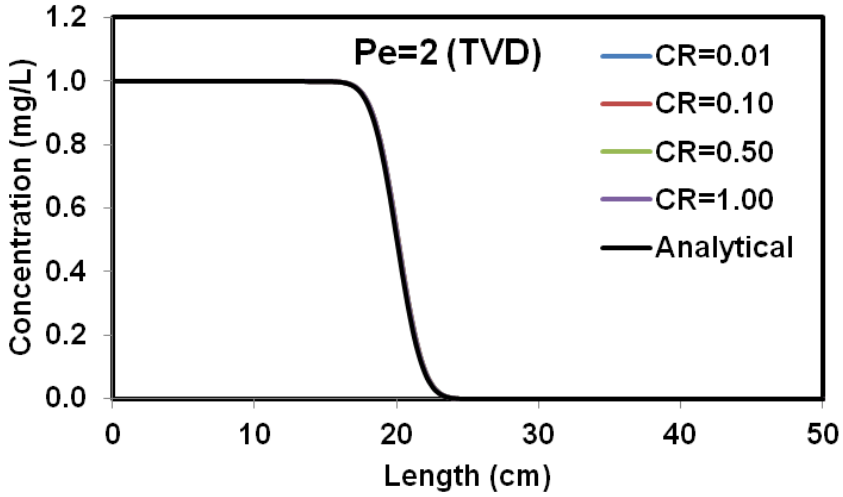


Figure 12. RT1D results for high Peclet number simulations with varying Courant number using the TVD advection and implict scheme (v=1cm/day, D=0.05 cm^2/day, dx=0.1cm)

3.2.3 ADVECTION DISPERSION AND REACTION MODULES

In this section, we present the results to test the program's stability under varying Peclet and Courant numbers in the presence of a first order decay constant for a single component. The simulations were compared with analytical solutions. For the high Peclet number simulations, the data from the first component of Bauer *et al.* (2001) was used and for low Peclet number

simulations, the date from the first component of Quezada *et al.* (2004) was used. Simulations were performed for different Courant numbers of 0.01, 0.1, 0.5 and 1.0. The parameters for these simulations are presented in Table 1.

	High	Low
Length (cm)	40	3000
Time (days)	50	3000
dx (cm)	0.4	5
Velocity (cm/day)	0.4	1
Dispersion Coefficient (cm^2/day)	0.08	10
Retardation	1	5.3
Decay constant (1/day)	0.075	7.00E-04

Table 1. Parameters for low and high Peclet number simulations

3.2.3.1 EXPLICIT ADVECTION AND IMPLICIT DISPERSION

Simulations were performed with a time step of 1, 0.5, 0.1 and 0.01 for high Peclet number simulations and 26.5, 13.25, 2.65 and 0.265 days for low Peclet number simulations to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 13 and 14 show the results for low and high Peclet number simulations respectively. It was observed from the figures that explicit scheme performed well with both high and low Peclet numbers. There was some numerical dispersion in the presence of high Peclet number. However, this is negligible.

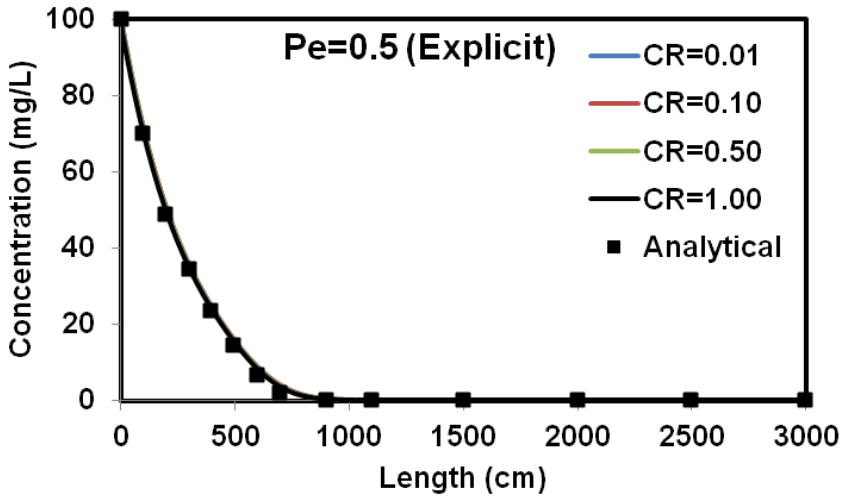


Figure 13. RT1D results for low Peclet number simulations with varying Courant number using the explicit advection and implict dispersion scheme (v=1 cm/day, D=10 cm^2/day, dx=5 cm, k=7.0E-4 day^{-1}, T=3000 days)

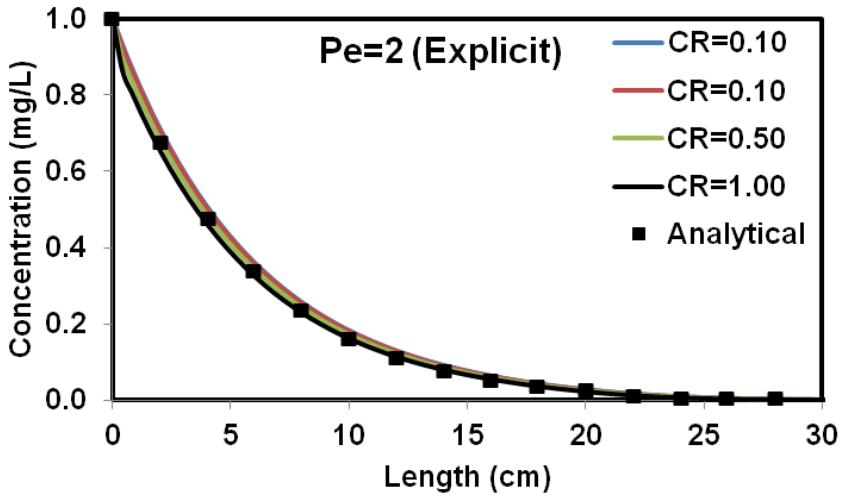


Figure 14. RT1D results for high Peclet number simulations with varying Courant number using the explicit advection and implict dispersion scheme (v=0.4 cm/day, D=0.08 cm^2/day, dx=0.4 cm, k=7.5E-2 day^{-1}, T=50 days)

3.2.3.2 FULLY IMPLICIT ADVECTION AND DISPERSION SCHEME

Simulations were performed with a time step of 1, 0.5, 0.1 and 0.01 for high Peclet number simulations and 26.5, 13.25, 2.65 and 0.265 days for low Peclet number simulations to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 15 and 16 show the results for low and high Peclet number simulations respectively. It was observed from the results that the fully implicit scheme performed well for both high and low Peclet numbers.

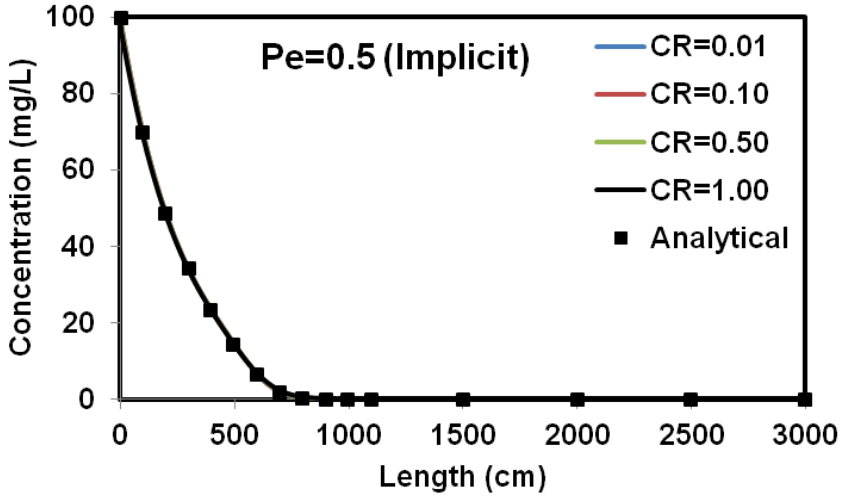


Figure 15. RT1D results for low Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=1 cm/day, D=10 cm^2/day, dx=5 cm, k=7.0E-4 day^{-1}, T=3000 days)

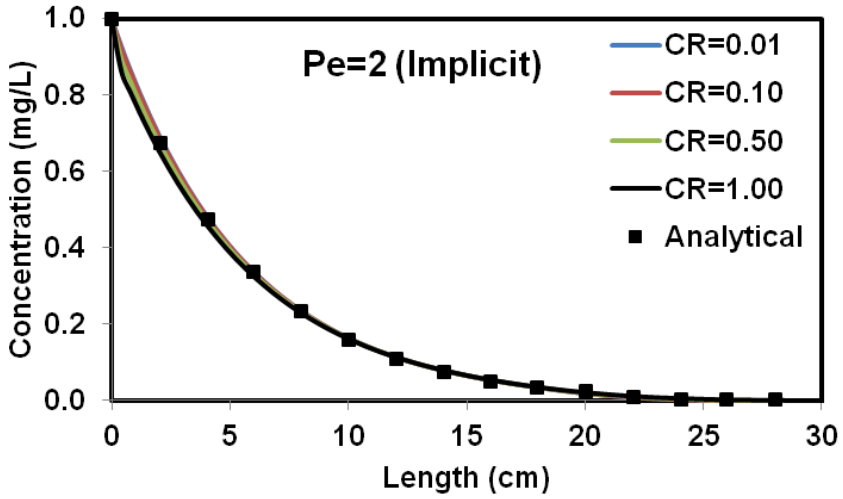


Figure 16. RT1D results for high Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=0.4 cm/day, D=0.08 cm^2/day, dx=0.4 cm, k=7.5E-2 day^{-1}, T=50 days)

3.2.3.3 TVD ADVECTION AND IMPLICIT DISPERSION

Simulations were performed with a time step of 1, 0.5, 0.1 and 0.01 for high Peclet number simulations and 26.5, 13.25, 2.65 and 0.265 days for low Peclet number simulations to generate Courant numbers of 1, 0.5, 0.1 and 0.01 respectively. Figure 17 and 18 show the results for low and high Peclet number simulations respectively.

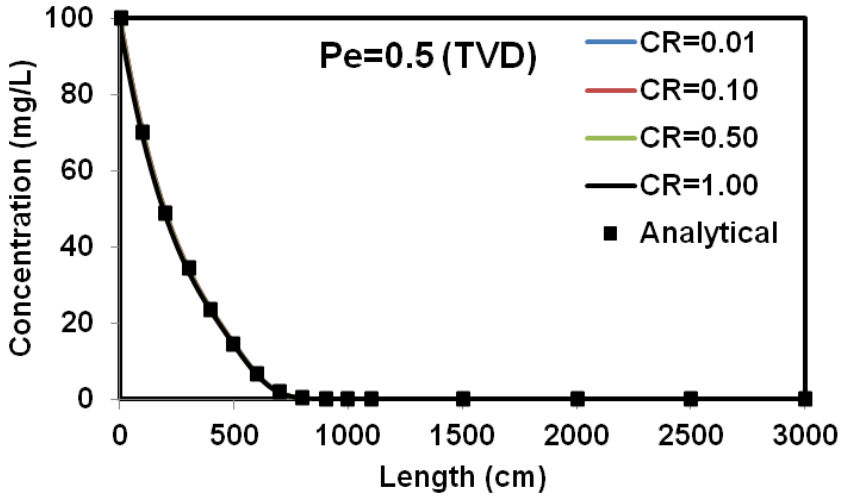


Figure 17. RT1D results for low Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=1 cm/day, D=10 cm^2/day, dx=5 cm, k=7.0E-4 day^{-1}, T=3000 days)

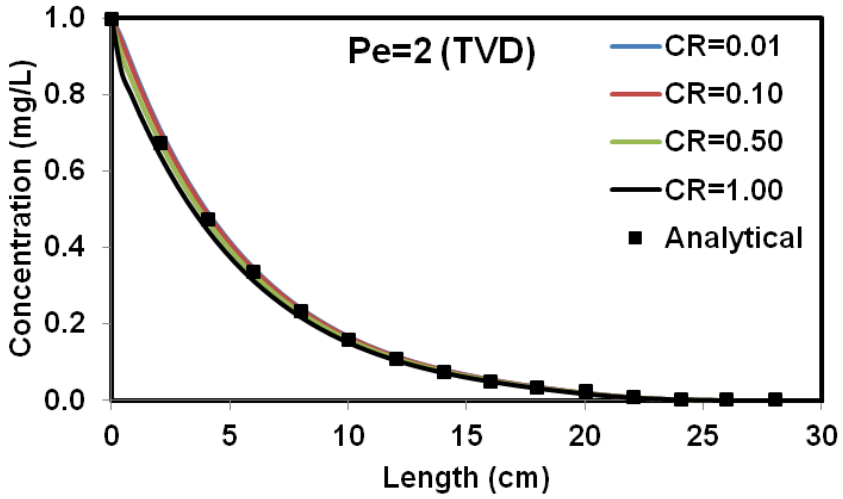


Figure 18. RT1D results for high Peclet number simulations with varying Courant number using the fully implicit advection dispersion scheme (v=0.4 cm/day, D=0.08 cm^2/day, dx=0.4 cm, k=7.5E-2 day^{-1}, T=50 days)

There was some numerical dispersion for very low courant numbers in the high Peclet number simulations but this was negligible and the results from RT1D matched the analytical solutions well.

3.3 LIST OF KINETIC REACTION PACKAGES

In the following section, we will present a discussion about the built-in reaction packages in the RT1D program. Each reaction package and its code form will be presented.

3.3.1 FIRST ORDER SEQUENTIAL DEGRADATION (RXNTYPE=1)

A generalized reactive transport equation for a single component first order decay is present below.

$$R\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - kC \qquad (19)$$

Where C is concentration of the mobile component, k is the first order decay constant (T^{-1}). The above equation simulates a tracer when the decay constant is set to zero. This reaction package could be written in the code form as follows:

dydt(1)=1/R(1)*RC(1)*Conc(1)

Where dydt(1) is the ordinary differential equation for the mobile component 1, R(1) is the retardation factor for component 1 and RC(1) is the user-set reaction parameter (k), Conc(1) is the aqueous concentration of the mobile component.

3.3.2 FOUR SPECIES COUPLED SEQUENTIAL DEGRADATION (RXNTYPE=2)

Quezada *et al.* (2004) presented the analytical solutions for a four species coupled sequential first order degradation reactions. The reaction equations simulate the transport and coupled decay of four mobile components. The governing equations are as follows:

$$R_1 \frac{\partial C_1}{\partial t} = -V \frac{\partial C_1}{\partial x} + D \frac{\partial^2 C_1}{\partial x^2} - k_1 C_1 \tag{20}$$

$$R_2 \frac{\partial C_2}{\partial t} = -V \frac{\partial C_2}{\partial x} + D \frac{\partial^2 C_2}{\partial x^2} + F_{c2/c1} Y_{c2/c1} k_1 C_1 - k_2 C_2 + F_{c2/c3} Y_{c2/c3} k_3 C_3 \tag{21}$$

$$R_3 \frac{\partial C_3}{\partial t} = -V \frac{\partial C_3}{\partial x} + D \frac{\partial^2 C_3}{\partial x^2} + F_{c3/c1} Y_{c3/c1} k_1 C_1 + F_{c3/c2} Y_{c3/c2} k_2 C_2 - k_3 C_3 \tag{22}$$

$$R_4 \frac{\partial C_4}{\partial t} = -V \frac{\partial C_4}{\partial x} + D \frac{\partial^2 C_4}{\partial x^2} + F_{c4/c2} Y_{c4/c2} k_2 C_2 + F_{c4/c3} Y_{c4/c3} k_3 C_3 - k_4 C_4 \tag{23}$$

Where R_i is the retardation factor; V the seepage velocity (LT^{-1}), D is the hydrodynamic dispersion coefficient (LT^{-2}), Y is the yield coefficient, F is the fraction, k (T^{-1}) is the first order decay constant. The above reaction equations could be written in code format as follows:

```
dydt(1) = -RC(1) * Conc(1) / R(1)
dydt(2) = (RC(11) * RC(5) * RC(1) * Conc(1) - RC(2) * Conc(2) + RC(12) * RC(6) * RC(3)
* Conc(3)) / R(2)
dydt(3) = (RC(13) * RC(7) * RC(1) * Conc(1) + RC(14) * RC(8) * RC(2) * Conc(2) - RC(3)
* Conc(3)) / R(3)
dydt(4) = (RC(14) * RC(9) * RC(2) * Conc(2) + RC(16) * RC(10) * RC(3) * Conc(3) - RC(4)
* Conc(4)) / R(4)
```

where dydt(i) is the expression for ODE for component i; i could be either 1, 2, 3 or 4; R(i) is the retardation factor for the component i; RC(i) is the user-set reaction parameters, Conc(i) is the concentration of the component i.

3.3.3 FOUR COMPONENT DECAY CHAIN (RXNTYPE=3)

Bauer et al., 2001 presented analytical solutions for the transport of a decay chain for in homogenous porous media. The reaction equations presented in the paper were used as a built-in reaction package for the RT1D. The reaction equations are as follows

$$R_1 \frac{\partial C_1}{\partial t} = -V \frac{\partial C_1}{\partial x} + D \frac{\partial^2 C_1}{\partial x^2} - k_1 C_1 \quad (24)$$

$$R_2 \frac{\partial C_2}{\partial t} = -V \frac{\partial C_2}{\partial x} + D \frac{\partial^2 C_2}{\partial x^2} + k_1 R_1 C_1 - k_2 R_2 C_2 \quad (25)$$

$$R_3 \frac{\partial C_3}{\partial t} = -V \frac{\partial C_3}{\partial x} + D \frac{\partial^2 C_3}{\partial x^2} + k_2 R_2 C_2 - k_3 R_3 C_3 \quad (26)$$

$$R_4 \frac{\partial C_4}{\partial t} = -V \frac{\partial C_4}{\partial x} + D \frac{\partial^2 C_4}{\partial x^2} k_3 R_3 C_3 - k_4 R_4 C_4 \quad (27)$$

Where R_i is the retardation factor; V the seepage velocity (LT^{-1}), D is the hydrodynamic dispersion coefficient (LT^{-2}), k_i (T^{-1}) is the first order decay constant. Further details of the model are available in Bauer et al., 2001. The code format for this reaction package is as follows:

```
dydt(1) = -RC(1) * Conc(1)
dydt(2) = (RC(1) * Conc(1) * R(1) - RC(2) * Conc(2) * R(2)) / R(2)
dydt(3) = (RC(2) * Conc(2) * R(2) - RC(3) * Conc(3) * R(3)) / R(3)
dydt(4) = (RC(3) * Conc(3) * R(3) - RC(4) * Conc(4) * R(4)) / R(4)
```

The description for the variables is similar to the reaction packages explained above.

3.3.4 MODIFIED MONOD KINETICS FOR TCE BIOAUGMENTATION (RXNTYPE=4)

Schaefer et al (2009) conducted batch experiments to study the bioaugmentation of TCE. They used Modified Monod kinetics to model these reactions. The reaction package for this model is as follows: (note that there are no advection dispersion terms as this is a batch system)

$$\frac{dC_{TCE}}{dt} = -\frac{1}{R_{TCE}} \left[\frac{q_{TCE} X C_{TCE}}{C_{TCE} + K_{TCE}} \right] \quad (28)$$

$$\frac{dC_{DCE}}{dt} = -\frac{1}{R_{DCE}} \left[\frac{q_{DCE} X C_{DCE}}{C_{DCE} + K_{DCE} \left(1 + \frac{C_{TCE}}{I_{TCE}} \right)} \right] + \frac{1}{R_{TCE}} \left[\frac{q_{TCE} X C_{TCE}}{C_{TCE} + K_{TCE}} \right] \quad (29)$$

$$\frac{dC_{VC}}{dt} = -\frac{1}{R_{VC}} \left[\frac{q_{VC} X C_{VC}}{C_{VC} + K_{VC} \left(1 + \frac{C_{TCE}}{I_{TCE}} + \frac{C_{DCE}}{I_{DCE}} \right)} \right] + \frac{1}{R_{DCE}} \left[\frac{q_{DCE} X C_{DCE}}{C_{DCE} + K_{DCE} \left(1 + \frac{C_{TCE}}{I_{TCE}} \right)} \right] \quad (30)$$

$$\frac{dX}{dt} = YX\left[\frac{1}{R_{TCE}}\frac{q_{TCE}C_{TCE}}{C_{TCE}+K_{TCE}} + \frac{1}{R_{DCE}}\frac{q_{DCE}C_{DCE}}{C_{DCE}+K_{DCE}\left(1+\frac{C_{TCE}}{I_{TCE}}\right)} + \frac{1}{R_{VC}}\frac{q_{VC}C_{VC}}{C_{VC}+K_{VC}\left(1+\frac{C_{TCE}}{I_{TCE}}+\frac{C_{DCE}}{I_{DCE}}\right)}\right] \quad (31)$$

Where C_i (mM) and X (cells/L) are the concentration of ith compound and biomass respectively; i can be either TCE, DCE and VC; q_i is the maximum biomass utilization rate, K_i is the half velocity coefficient of the compound, I is the competition coefficient, R_i is the retardation due to the presence of air-gap. For further details about the model and the experimental methods, refer to Schaefer et al (2009). The code form of this reaction package is given below:

```
mTCE = ((RC(4) * Conc(1)) / (Conc(1) + RC(1)))
mDCE = ((RC(5) * Conc(2)) / (Conc(2) + RC(2) * (1 + (Conc(1) / RC(7)))))
mVC = ((RC(6) * Conc(3)) / (Conc(3) + RC(3) * (1 + (Conc(1) / RC(7)) + (Conc(2) /
RC(8)))))

dydt(1) = (-1 / R(1)) * Conc(5) * mTCE
dydt(2) = -Conc(5) * (mDCE / R(2) - mTCE / R(1))
dydt(3) = -Conc(5) * (mVC / R(3) - mDCE / R(2))
dydt(4) = Conc(5) * mVC / R(3)
dydt(5) = (RC(10) * Conc(5)) * (mTCE / R(1) + mDCE / R(2) + mVC / R(3))
```

To simpify the equations, we have defined three different variables (mTCE, mDCE and mVC) to define the Monod terms for each component.

3.3.5 RATE LIMITED SORPTION (RXNTYPE=5)

In case of non-equilibrium conditions, the sorption is controlled by a mass-transfer coefficient (ξ). When the ξ value is really low, the plume acts like tracer because there is no sorption and when the ξ value is really high, the plume acts like a retarded plume due to the linear sorption. This kind of rate-limited sorption kinetics can be modeled using the following reaction package:

$$\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \xi\left(C - \frac{S}{K_d}\right) - kC \quad (32)$$

$$\frac{dS}{dt} = \frac{\varphi\xi}{\rho}\left(C - \frac{S}{K_d}\right) \quad (33)$$

Where C is the concentration of mobile phase (mg/L), S is the concentration of the immobile phase (mg/mg), k is the aqueous phase decay constant (1/day), K_d (L/mg) is the linear sorption constant, φ is the porosity, ρ is the bulk density of the soil (mg/L). The code form of this reaction package could be written as follows:

```
dydt(1) = -RC(2) * (Conc(1) - (Conc(2) / RC(3))) - RC(5) * Conc(1)
dydt(2) = (RC(4) / RC(1)) * RC(2) * (Conc(1) - (Conc(2) / RC(3)))
```

3.3.6 DENITRIFICATION (RXNTYPE=6)

Clement et al (1997) studied the effects of denitrifying conditions on the growth and transport of bacteria in a porous media column under two substrate loading conditions. A numerical model was developed to generate the breakthrough profiles of bacterial cells and substrates. A first order attachment and detachment model was used to describe the exchange processes between mobile and immobile-phase bacterial cells. This reaction package considered three mobile components namely nitrate, acetate and aqueous-phase bacteria, and one immobile component namely immobile bacteria. The reaction package used in the problem is given below:

$$\frac{\partial C_N}{\partial t} = -V\frac{\partial C_N}{\partial x} + D\frac{\partial^2 C_N}{\partial x^2} - r_N X_a - \frac{r_N X_s \rho}{n} \quad (34)$$

$$\frac{\partial C_A}{\partial t} = -V\frac{\partial C_A}{\partial x} + D\frac{\partial^2 C_A}{\partial x^2} - r_A X_a - \frac{r_A X_s \rho}{n} \quad (35)$$

$$\frac{\partial X_a}{\partial t} = -V\frac{\partial X_a}{\partial x} + D\frac{\partial^2 X_a}{\partial x^2} + r_X X_a - K_{at} X_a + \frac{K_{de} X_s \rho}{n} \quad (36)$$

$$\frac{dX_s}{dt} = r_X X_s - K_{de} X_s + \frac{n K_{at} X_a}{\rho} \quad (37)$$

Where C_N, C_A, X_a and X_s are concentrations (mg/L) of nitrate, acetate, aqueous-phase bacteria and immobile-phase bacteria (mg/mg), respectively. The parameters K_{at} (day^{-1}) and K_{de} (day^{-1}) are the attachment and detachment coefficients of mobile and immobile phase bacteria, respectively; n is the porosity of soil; and ρ is the bulk density of the soil (mg/L). The rate expression r_N is the nitrate utilization rate described by the Monod kinetics $r_N = q_{max}\left[\frac{C_N}{K_N + C_N}\right]\left[\frac{C_A}{K_A + C_A}\right]$ Where q_{max} is the maximum nitrate utilization rate (mg nitrate/ mg biomass-day), K_N is the half saturation coefficient for nitrate (mg/L); K_A is the half saturation coefficient for acetate (mg/L). The specific utilization rate of acetate (r_A) and biomass growth rate (r_X) are given by the expressions: $r_A = Y_{A/N} r_N$ and $r_X = Y_{X/N} r_N - K_d$, where $Y_{A/N}$ and $Y_{X/N}$ are the yield coefficients for acetate and biomass, respectively, and K_d is the cell decay rate coefficient (day^{-1}). The code format for this reaction package could be written as follows:

```
rN = RC(3) * (Conc(1) / (RC(1) + Conc(1))) * (Conc(2) / (RC(2) + Conc(2)))
rA = RC(6) * rN
rX = RC(7) * rN - RC(5)
dydt(1) = -rN * Conc(3) - (rN * Conc(4) * RC(9) / RC(10))
dydt(2) = -rA * Conc(3) - (rA * Conc(4) * RC(9) / RC(10))
```

dydt(3) = rX * Conc(3) - RC(4) * Conc(3) + (RC(8) * Conc(4) * RC(9) / RC(10))
dydt(4) = rX * Conc(4) - RC(8) * Conc(4) + (RC(10) * RC(4) * Conc(3) / RC(9))

3.3.7 BIODEGRADATION OF CARBON TETRACHLORIDE (RXNTYPE=7)

Phanikumar et al (2004) studied the biodegradation of carbon tetrachloride (CT) in the presence of bacteria. The transport problem considered the following four mobile components: carbon tetrachloride, acetate, nitrate, and mobile-phase bacteria. The two immobile phase components are: sorbed carbon tetrachloride and immobile-phase bacteria. The reaction package for this problem is as follows: (note that the advection-dispersion terms are omitted here for brevity)

$$\left(1+\frac{\rho f K_d}{\varphi}\right)\frac{dC_{CT}}{dt} = -k' C_{CT}(X_M + X_{IM}) - \frac{\rho\kappa}{\varphi}\left[(1-f)K_d C_{CT} - S_{CT}\right] \quad (38)$$

$$R_a \frac{dC_a}{dt} = -\frac{\mu_{max} M_a M_n}{Y_a}(X_M + X_{IM}) \quad (39)$$

$$R_n \frac{dC_n}{dt} = -\frac{\mu_{max} M_a M_n}{Y_n}(X_M + X_{IM}) - \left[\frac{b_{KC}}{Y_{nb}}(1-M_a) + \gamma M_n\right](X_M + X_{IM}) \quad (40)$$

$$\frac{dX_M}{dt} = \left[\mu_{max} M_a M_n - b_{KC}(1-M_a) - K_{at}\right]X_M + K_{de}(1-M_a)X_{IM} \quad (41)$$

$$\frac{dS_{CT}}{dt} = \kappa\left[(1-f)K_d C_{CT} - S_{CT}\right] \quad (42)$$

$$\frac{dX_{IM}}{dt} = \left[\mu_{max} M_a M_n - b_{KC}(1-M_a) - K_{de}(1-M_a)\right]X_{IM} + K_{at} X_M \quad (43)$$

Where f is the fraction of equilibrium sites, b_{KC} is the microbial decay rate (day^{-1}), K_{at} is the attachment coefficient (day^{-1}), K_{de} is the detachment coefficient (day^{-1}), k` is the CT reaction rate (day^{-1}), γ is the nitrate reaction rate (day^{-1}), κ is the kinetic desorption rate (day^{-1}), μ_{max} is the maximum specific growth rate (day^{-1}), Y_a, Y_n and Y_{nb} are the yield rates of acetate, nitrate and biomass respectively; C_{CT}, C_a, C_n and S_{CT} are the aqueous concentrations of carbon tetrachloride, acetate, nitrate and the sorbed concentration of carbon tetrachloride, respectively; X_M and X_{IM} are the concentrations of mobile and immobile bacteria, respectively. Also, M_a and M_n are the Monod terms for acetate and nitrate reactions, respectively, and given by the expressions:

$M_a = \frac{C_a}{K_{sa} + C_a}$ and $M_n = \frac{C_n}{K_{sn} + C_n}$ where K_{sa} and K_{sn} are the half saturation coefficients of acetate and nitrate utilization reactions, respectively. The kinetic equations (38) to (40) describe biodegradation of carbon tetrachloride, utilization of an electron donor (acetate), and an electron acceptor (nitrate). Equation (41) describes the growth, decay, and attachment of the mobile phase bacteria, equation (42) describes the sorption of carbon tetrachloride using a two-site sorption model, and equation (43) describes the growth, decay, and detachment of immobile-phase bacteria. The code format for this reaction package could be written as follows:

```
Ma = Conc(2) / (RC(6) + Conc(2))
Mn = Conc(3) / (RC(10) + Conc(3))

dydt(1) = (-RC(14) * Conc(1) * (Conc(4) + Conc(6)) - (RC(4) * RC(7) / RC(15) * ((1 - RC(5)) * RC(2) * Conc(1) - Conc(5)))) / R(1)
dydt(2) = -(RC(11) * Ma * Mn / RC(8)) * (Conc(4) + Conc(6))
dydt(3) = -(RC(11) * Ma * Mn / RC(12)) * (Conc(4) + Conc(6)) - (RC(1) / RC(16) * (1 - Ma) + RC(3) * Mn) * (Conc(6) + Conc(4))
dydt(4) = (RC(11) * Ma * Mn - RC(1) * (1 - Ma) - RC(9)) * Conc(4) + RC(13) * (1 - Ma) * Conc(6)
dydt(5) = RC(7) * ((1 - RC(5)) * RC(2) * Conc(1) - Conc(5))
dydt(6) = (RC(11) * Ma * Mn - RC(1) * (1 - Ma) - RC(13) * (1 - Ma)) * Conc(6) + RC(9) * Conc(4)
```

3.3.8 USER DEFINED REACTION PACKAGE (RXNTYPE= 10)

RT1D is best utilized when the user supplies their reaction packages. To access this mode, the user is required to open the code and search for the term "RXN PACKAGE" without quotes. This will take the user to the *UsrRxnPkg()* subroutine in the program where the reaction package can be set. Four-species sequential first order decay is set by default and this can be modified to the user's convenience. The ordinary differential equation for the first species is dydt(1) and the concentration of the first species is Conc(1), the retardation is R(1) and RC(1) is the first reaction parameter and so on. Therefore, the equation for a first order decay of a single species can be written as: dydt(1)= -RC(1)*Conc(1) where RC(1) is the first order decay constant of the first species set by the user in the spreadsheet. Several example reaction packages are shown in the section above. These could be used as an example to program your own reaction packages. The reaction terms could be either defined inside the subroutine or outside the spreadsheet. It is recommended that the reaction terms be defined in spreadsheet so they could be changed quickly without having to open the code each time to modify these variables.

4. EXAMPLE PROBLEMS

4.1 EXAMPLE-1: REACTION PACKAGE #1

In this example problem, we will learn to use the reaction package #1. This reaction package simulates the first order decay of a single mobile component. We will use this reaction package to simulate a simple tracer transport and a reactive transport problem with a first order decay constant of 0.075 day^{-1}

1. Input the advection-dispersion parameters for this problem as shown in Figure 19.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	40	m	
4		Total Time	50	day	
5		Pulse Time	50	day	
6		delx	1	m	
7		delt	1	day	
8		Velocity	0.4	m/day	
9		Dispersion coefficient	0.08	m2/day	
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					
15	Kinetics Type Problem (SO = 1 & 2)			Geochemistry Type Problem (SO = 3 & 4)	
16	# Mobile Components	1		# Components	N/A
17	# Immobile Components	0		# Species	N/A
18	RXN Package #	1		# Fixed Comp Concentrations	N/A
19	ODE Solver Type	1		# Aqueous Concentrations	N/A
20	# Reaction Parameters	1		# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

Figure 19. Advection-dispersion parameters for the example problem 1

2. This reaction package is set up for one species only and therefore, the number of mobile components in cell B16 is set to 1.
3. Select the reaction package number as 1 in B18.
4. We will use the Runge-kutta Fehlberg ODE solver for this solver and the short code for this solver is set in B19.
5. We need to set the k value for this reaction package and hence we will set "# Reaction Parameters" as 1
6. Press the "Generate Input Template" button. This will clear everything below and an input sheet will be generated as shown in Figure 20. Note that the program automatically sets the geochemistry type problem values to "N/A" to show that we're running a kinetic type problem.

27	Component Name	R	Initial	Boundary
28	Mobile Component 1	1	0	1
29				
30	Reaction Parameter Label	Value		
31	Reaction Term 1	0		

Figure 20. Component initial and boundary conditions along with the kinetic parameters

7. The initial concentration in the column is 0 and a constant concentration pulse of 1 mg/L is supplied at the inlet for the entire duration of the simulation. Therefore, we will set the boundary condition as 1. The retardation factor for this example will be set as 1.
8. The k value can be changed to any desired value in the B31. For this example, we have used two different values (0.075 and 0). When k is set to 0, the plume acts like a tracer.
9. Press the solve button to display the spatial variation of concentration in Sheet 2 and the breakthrough concentrations at the outlet are displayed in Sheet 3. The results for this example for both k values are presented in Figure 21.

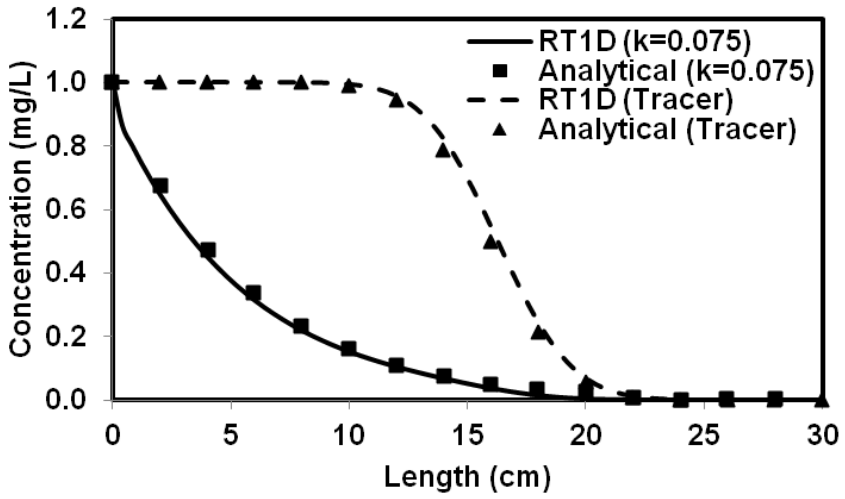


Figure 21. Results for two different k values for example problem 1

4.2 EXAMPLE-2: REACTION PACKAGE #2

In this example problem, we will learn to use the reaction package #2 which simulates the four species first order sequential decay as described in section 3.3.2

1. Input the advection-dispersion and reaction parameters as shown in Figure 22. This information can be obtained from Quezada *et al.* (2004)]
2. This is a four species problem, so we will set the number of mobile components in cell B16 as 4 and the reaction package we will use for this problem is 2.
3. The ODE solver can be either 0 or 1 and this shouldn't change the results by much
4. There are a total of 16 reaction parameters for this problem and the values for these reaction parameters are available in Figure 23.

5. The retardation factors for the components are 1, 2, 3 and 4 respectively and the initial concentration for all the components was zero. The inlet was supplied with a constant concentration of 1 mg/L of Component-1 for the entire duration of the simulation.
6. The results from this simulation are shown in Figure 24.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	40	m	
4		Total Time	50	day	
5		Pulse Time	50	day	
6		delx	1	m	
7		delt	1	day	
8		Velocity	0.4	m/day	
9		Dispersion coefficient	0.08	m2/day	
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					
15		Kinetics Type Problem (SO = 1 & 2)		Geochemistry Type Problem (SO = 3 & 4)	
16		# Mobile Components	4	# Components	N/A
17		# Immobile Components	0	# Species	N/A
18		RXN Package #	2	# Fixed Comp Concentrations	N/A
19		ODE Solver Type	0	# Aqueous Concentrations	N/A
20		# Reaction Parameters	16	# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

Figure 22. The advection-dispersion parameters for the example problem 2

27	Component Name	R	Initial	Boundary
28	Component 1	1.00	0	1
29	Component 2	2.00	0	0
30	Component 3	3.00	0	0
31	Component 4	4.00	0	0
32				
33	Reaction Parameter Label	Value		
34	k1	0.075		
35	k2	0.05		
36	k3	0.02		
37	k4	0.045		
38	Yc2/c1	1.00E+00		
39	Yc2/c3	1.00E+00		
40	Yc3/c1	1.00E+00		
41	Yc3/c2	1.00E+00		
42	Yc4/c2	1.00E+00		
43	Yc4/c3	1.00E+00		
44	Fc2/c1	0.75		
45	Fc2/c3	0.9		
46	Fc3/c1	0.25		
47	Fc3/c2	0.5		
48	Fc4/c2	0.5		
49	Fc4/c3	0.1		

Figure 23. Complete list of reaction parameters for the example problem 2

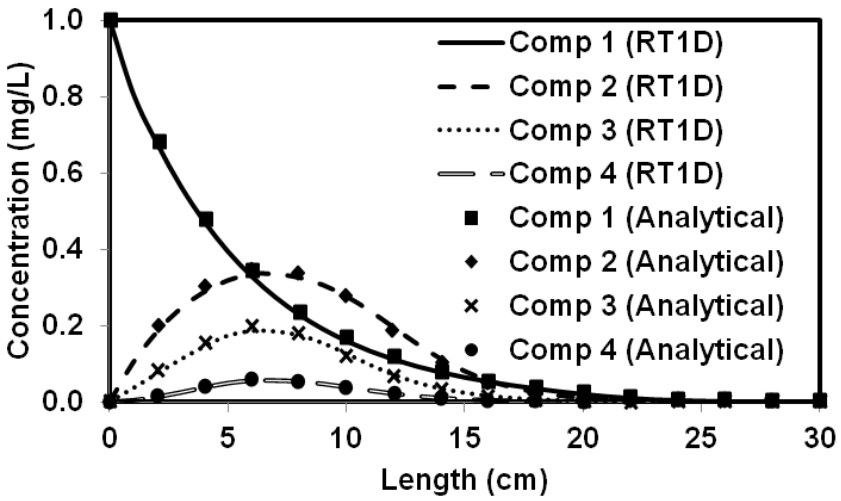


Figure 24. Results for the example problem 2

4.3 EXAMPLE-3: REACTION PACKAGE #3

In this example, we will learn to use the reaction package #3, which describes the transport of a decay chain of a four component system.

1. Input the advection dispersion parameters for the problem as shown in Figure 25.
2. There are a total of 4 mobile components and the reaction package for this example is built into the RT1D model as option 3.
3. There are a total of 4 first order decay constants for each mobile component and the ODE solver type can be either 0 or 1.
4. Press the "Generate Input Template" button to generate a table to input all the reaction parameters
5. The column is supplied with 100 mg/L of Component-1 for the entire duration of the simulation at the inlet and there was no initial concentration before the beginning of the simulation, so set the initial condition for all the components as 0 as shown in Figure 26.
6. Input the retardation factors and the first order decay constant for each component as shown in Figure 25. Press the solve button to generate the solutions.
7. The results for this simulation are shown in Figure 27.

	A	B	C	D	E
1		Advection-Dispersion Parameters			1
2		Parameter Name	Value	Units	26.5
3		Length	3000	m	
4		Total Time	3000	day	
5		Pulse Time	3000	day	
6		delx	5	m	
7		delt	1	day	
8		Velocity	1	m/day	0.037735849
9		Dispersion coefficient	10	m2/day	0.5
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					

15	Kinetics Type Problem (SO = 1 & 2)	
16	# Mobile Components	4
17	# Immobile Components	0
18	RXN Package #	3
19	ODE Solver Type	0
20	# Reaction Parameters	4
21		

Geochemistry Type Problem (SO = 3 & 4)	
# Components	N/A
# Species	N/A
# Fixed Comp Concentrations	N/A
# Aqueous Concentrations	N/A
# Sorbed Concentrations	N/A
SCM TYPE	N/A

Figure 25. Advection-dispersion parameters for example problem 3

26				
27	Component Name	R	Initial	Boundary
28	Component 1	5.30	0	100
29	Component 2	1.90	0	0
30	Component 3	1.20	0	0
31	Component 4	1.30	0	0
32				
33	Reaction Parameter Label	Value		
34	Reaction Term 1	7.00E-04		
35	Reaction Term 2	5.00E-04		
36	Reaction Term 3	4.50E-04		
37	Reaction Term 4	3.80E-04		

Figure 26. Reaction parameters for example problem 3

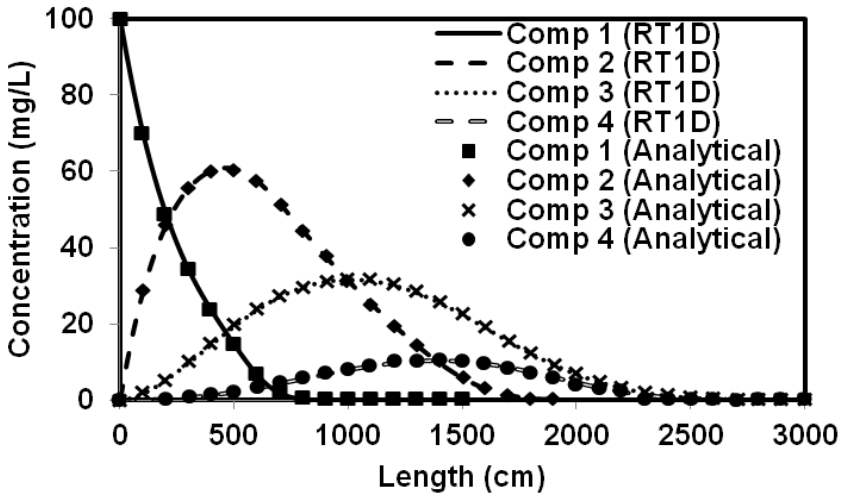


Figure 27. Reaction parameters for example problem 3

4.4 EXAMPLE-4: REACTION PACKAGE #4

This is the reaction package that describes the bioaugmentation of TCE using *Dehalococcoides Sp*. in a batch mode. We will run this example with the simulation option 1 to exclude the transport part of the code.

1. Input the parameters for the example problem as shown in Figure 28. The model automatically ignores advection dispersion parameters if the simulation option is set to 1.
2. The number of components in this example problem is five and this is a batch kinetics problem so we will consider all the components as immobile components.
3. The reaction package number for this problem is 4 and there are a total of 10 reaction parameters that need to be input by the user

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	1	cm	
4		Total Time	12	day	
5		Pulse Time	12	day	
6		delx	1	cm	
7		delt	0.01	day	0.01
8		Velocity	1	cm/day	
9		Dispersion coefficient	1	cm2/day	
10		Adv-Disp Type	0		
11		Simulation Option (SO)	1		
12					
13					
14					
15	Kinetics Type Problem (SO = 1 & 2)			Geochemistry Type Problem (SO = 3 & 4)	
16	# Mobile Components	0		# Components	N/A
17	# Immobile Components	5		# Species	N/A
18	RXN Package #	0		# Fixed Comp Concentrations	N/A
19	ODE Solver Type	1		# Aqueous Concentrations	N/A
20	# Reaction Parameters	10		# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

Figure 28. Advection-dispersion parameters for the example problem 4

4. The Monod parameters that need to be input are shown in Figure 29.
5. Schaefer *et al.* (2009) used retardation factor that was calculated due to the presence of air-gap in the batch experiments. This is not similar to the retardation caused due to the linear sorption in transport experiments. However, for convenience, the R values used in paper are input in the R column for the components.
6. This is a batch experiment, so there is no need to set a boundary condition. The program ignores the boundary condition even if it is set by the user. The initial concentrations of the components should be input in the "Initial" column.
7. Input all the Monod parameters as shown in Figure 29. The reaction parameter labels are set for the user's convenience and are ignored by the program.
8. Press the solve button and the results for the batch simulations are presented in Sheet 3 and the results for this simulation are shown in Figure 30.

	Component Name	R	Initial	Boundary
28	TCE	1.30	0.08	
29	DCE	1.17	0	
30	VC	2.10	0	
31	Ethene	1.00	0	
32	DHC	1.00	2.80E+10	
33				
34	Reaction Parameter Label	Value		
35	kTCE	3.20E-03		
36	kDCE	2.00E-03		
37	kVC	1.40E-02		
38	qTCE	1.30E-12		
39	qDCE	7.00E-13		
40	qVC	1.40E-12		
41	iTCE	1.00E+06		
42	iDCE	5.20E-03		
43	iVC	1.00E+06		
44	yield	4.40E+09		

Figure 29. Monod parameters for example problem 4

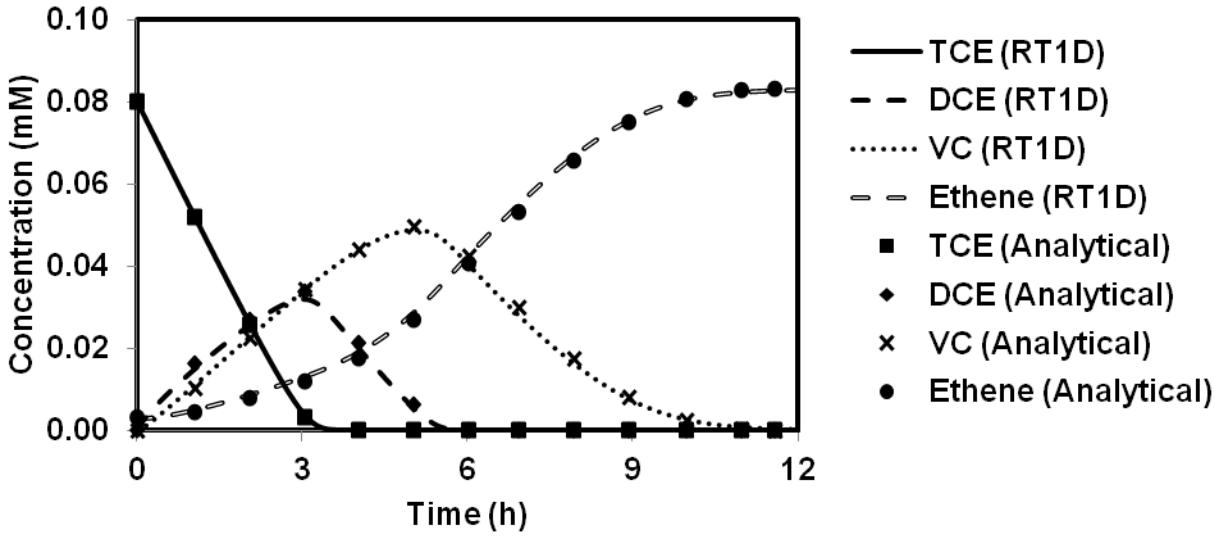


Figure 30. Results for example problem 4

4.5 EXAMPLE-5: REACTION PACKAGE #5

This is the first benchmark problem presented in Torlapati and Clement (2012).

1. Input the advection-dispersion parameters as shown in Figure 31
2. The reaction package for this problem is 5 and the simulation option is 2 because this is coupled with transport

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	40	cm	
4		Total Time	50	day	
5		Pulse Time	50	day	
6		delx	0.25	cm	
7		delt	0.01	day	
8		Velocity	0.53	cm/day	
9		Dispersion coefficient	0.08	cm2/day	
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					
15		Kinetics Type Problem (SO = 1 & 2)		Geochemistry Type Problem (SO = 3 & 4)	
16		# Mobile Components	1	# Components	N/A
17		# Immobile Components	1	# Species	N/A
18		RXN Package #	5	# Fixed Comp Concentrations	N/A
19		ODE Solver Type	1	# Aqueous Concentrations	N/A
20		# Reaction Parameters	5	# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

Figure 31. Advection-dispersion parameters for example problem 5

27	Component Name	R	Initial	Boundary
28	Mobile Phase	1	0	1
29	Immobile Phase	1	0	0
30				
31	Reaction Parameter Label	Value		
32	rho	1600		
33	Xi	2		
34	Kd	1.88E-04		
35	phi	0.3		
36	K	0		

Figure 32. Reaction parameters for example problem 5

3. There is one mobile component and a corresponding immobile phase component and there are a total of 5 reaction parameters that can be set by the user. Press the "generate input template" button once the parameters have been set.
4. Input the reaction parameters and the initial and boundary conditions as shown in Figure 18. The concentration of both components before the beginning of the experiment is zero and a concentration pulse of 1 mg/L was supplied near the inlet for the entire duration of the experiment.
5. Press the solve button to generate the results in Sheet 2 and 3. The results for the above parameters are shown in Figure 33.

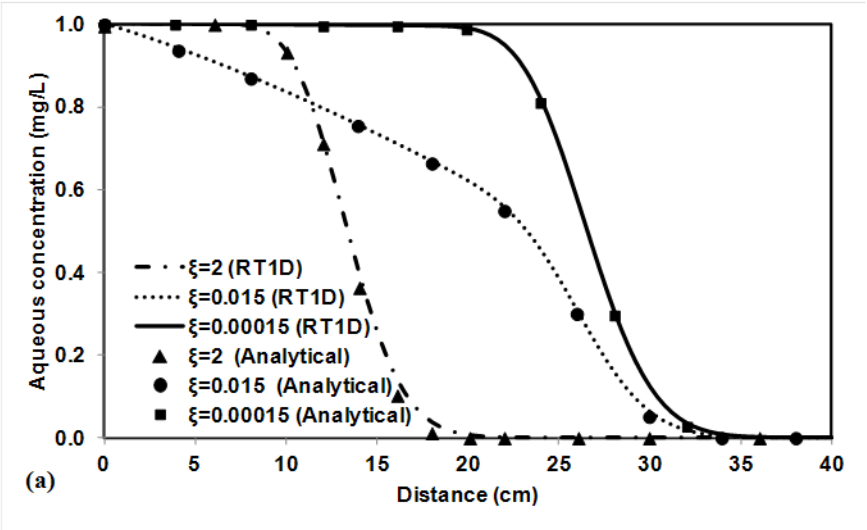


Figure 33. Results for example problem 5 for varying mass transfer coefficients

4.6 EXAMPLE-6: REACTION PACKAGE #6

This is the second benchmark problem in the Torlapati and Clement (2012) paper. The code form of this reaction package is as follows:

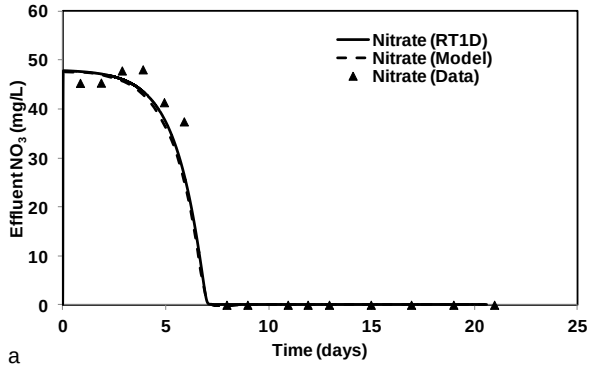
1. Input the advection dispersion parameters as shown in Figure 34. Please note that this is a computationally intensive problem and will take a substantial amount of time for the simulation to finish. The excel program will be unresponsive during this process, please don't close the program.
2. There are three mobile component and one immobile phase component in this problem. There are about 10 reaction parameters that are need to be set by the user.
3. The reaction package for this problem is 6. Press the "generate input template" button and input the reaction parameters as shown in Figure 35.
4. The parameters set here are for high flow experimental dataset from the paper. There is a constant supply of nitrate and acetate throughout the length of the experiment from the inlet and there was an initial concentration of aqueous and solid biomass which continue to grow.
5. The results from the RT1D simulations are shown in Figure 36 (a) and (b)

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	50	cm	
4		Total Time	10	day	
5		Pulse Time	10	day	
6		delx	1	cm	
7		delt	0.0001	day	
8		Velocity	1890.909091	cm/day	
9		Dispersion coefficient	1890.909091	cm2/day	
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					
15	Kinetics Type Problem (SO = 1 & 2)			Geochemistry Type Problem (SO = 3 & 4)	
16	# Mobile Components	3		# Components	N/A
17	# Immobile Components	1		# Species	N/A
18	RXN Package #	6		# Fixed Comp Concentrations	N/A
19	ODE Solver Type	1		# Aqueous Concentrations	N/A
20	# Reaction Parameters	10		# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

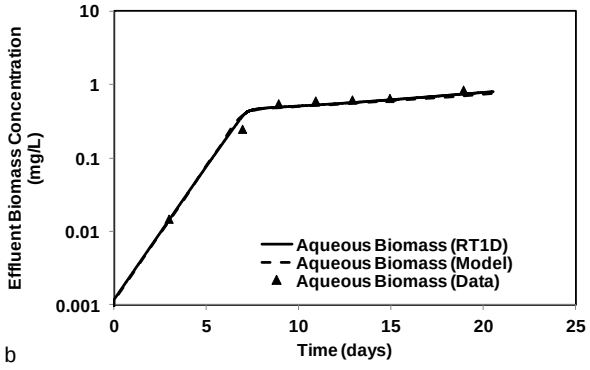
Figure 34. Advection-dispersion parameters for the example problem 6

26				
27	Component Name	R	Initial	Boundary
28	Nitrate	1	0	48
29	Acetate	1	0	58
30	Aqueous Biomass	1	1E-15	0
31	Solid Biomass	1	0.0000003	0
32				
33	Reaction Parameter Label	Value		
34	Kn	0.66		
35	Ka	1.2		
36	qmax	7.21		
37	Katt	288		
38	Kd	0.06		
39	Ya/n	0.84		
40	Yx/n	0.13		
41	kdet	0.32		
42	bulk density (rho)	1560000		
43	porosity	0.44		

Figure 35. Kinetic parameters for the example problem 6



a



b

Figure 36. (a) Nitrate concentration for the high flow experiment, (b) Aqueous biomass concentration comparison for the high flow experiment

4.7 EXAMPLE-7: REACTION PACKAGE #7

This is the benchmark problem 3 from Torlapati et al., 2012. This reaction package describes the biodegradation of carbon tetrachloride in the presence of nitrate and acetate. The code form of the reaction package can be written as follows

1. Input the advection-dispersion parameters for the example problem as shown in Figure 37. There are a total of 4 mobile components and 2 immobile components for this problem
2. The reaction package for this problem is 7 and the user needs to input 16 reaction terms.
3. Press the "generate input template" button
4. Input the retardation factor, initial condition and boundary condition as shown in the Figure 38.
5. Due to the presence of a slug injection zone, as described in Phanikumar *et al.* (2002), the initial condition for an 11cm section of the column is different from the rest of the column.
    a. To add this initial condition to the program would require editing the initial condition subroutine called setinit()
    b. Find this subroutine and uncomment the lines of under the "this is needed for initial condition in Phanikumar *et al.* (2002).
    c. Copy/paste the information available in Table 2 in "Sheet 4" in the spreadsheet. Create a "Sheet 4" if it is not available. The uncommented code-segment looks for the initial condition for the slug-injection zone in the Sheet 4.
6. Press the solve button and simulation results are available in Sheets 2 & 3. The results for this example problem are shown in Figure 39.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	200	cm	
4		Total Time	4	day	
5		Pulse Time	4	day	
6		delx	1	cm	
7		delt	0.001	day	
8		Velocity	10	cm/day	
9		Dispersion coefficient	2	cm2/day	
10		Adv-Disp Type	2		
11		Simulation Option (SO)	2		
12					
13					
14					
15	Kinetics Type Problem (SO = 1 & 2)			Geochemistry Type Problem (SO = 3 & 4)	
16	# Mobile Components	4		# Components	N/A
17	# Immobile Components	2		# Species	N/A
18	RXN Package #	7		# Fixed Comp Concentrations	N/A
19	ODE Solver Type	0		# Aqueous Concentrations	N/A
20	# Reaction Parameters	16		# Sorbed Concentrations	N/A
21				SCM TYPE	N/A

Figure 37. Advection-dispersion parameters for example problem 7

Slug injection zone	CT	Acetate	Nitrate	Mobile bacteria	Solid CT	Immobile bacteria
0	0.1	1650	42	11.8	0.000000028	0
1	0.1	1650	42	11.8	0.000000028	0
2	0.1	1650	42	11.8	0.000000028	0
3	0.1	1650	42	11.8	0.000000028	0
4	0.1	1650	42	11.8	0.000000028	0
5	0.1	1650	42	11.8	0.000000028	0
6	0.1	1650	42	11.8	0.000000028	0
7	0.1	1650	42	11.8	0.000000028	0
8	0.1	1650	42	11.8	0.000000028	0
9	0.1	1650	42	11.8	0.000000028	0
10	0.1	1650	42	11.8	0.000000028	0
11	0.1	1650	42	11.8	0.000000028	0

Table 2. Initial condition for the slug injection zone for example problem 7

27	Component Name	R	Initial	Boundary
28	CT	1.793716857	0.13	0.145
29	Acetate	1	0	0
30	Nitrate	1	42	42
31	Mobile bacteria	1	0	0
32	Solid CT		2.80E-08	0
33	Immobile bacteria		0.00E+00	0
34				
35	Reaction Parameter Label	Value		
36	bKC	0.221		
37	Kd	3.90E-07		
38	gamma	5.73		
39	bulk density	1.63E+06		
40	f	0.437		
41	Ksa	1		
42	Kappa	0.36		
43	Ya	0.4		
44	Kat	0.9		
45	Ksn	12		
46	umax	3.11		
47	Yn	0.25		
48	Kde	0.043		
49	k'	0.189		
50	porosity	0.35		
51	Ynb	0.46		

Figure 38. Kinetic parameters for example problem 7

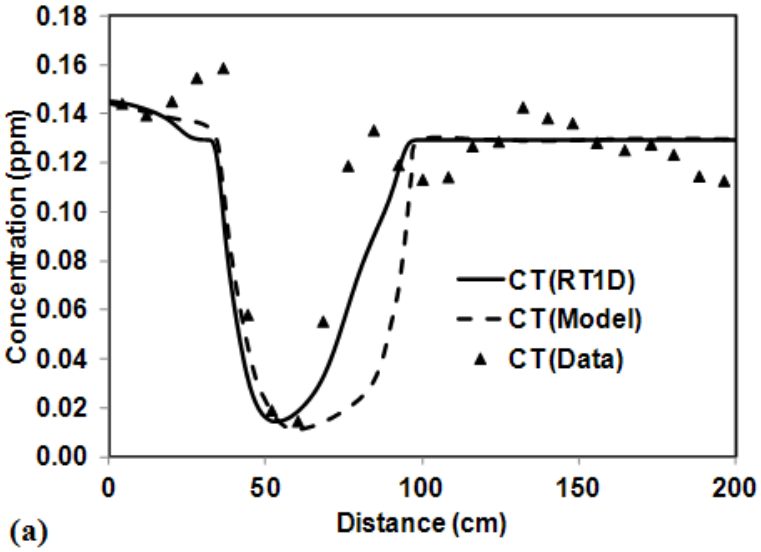


Figure 39. Carbon tetrachloride concentration after 4 days

4.8 EXAMPLE-8: SURFACE COMPLEXATION

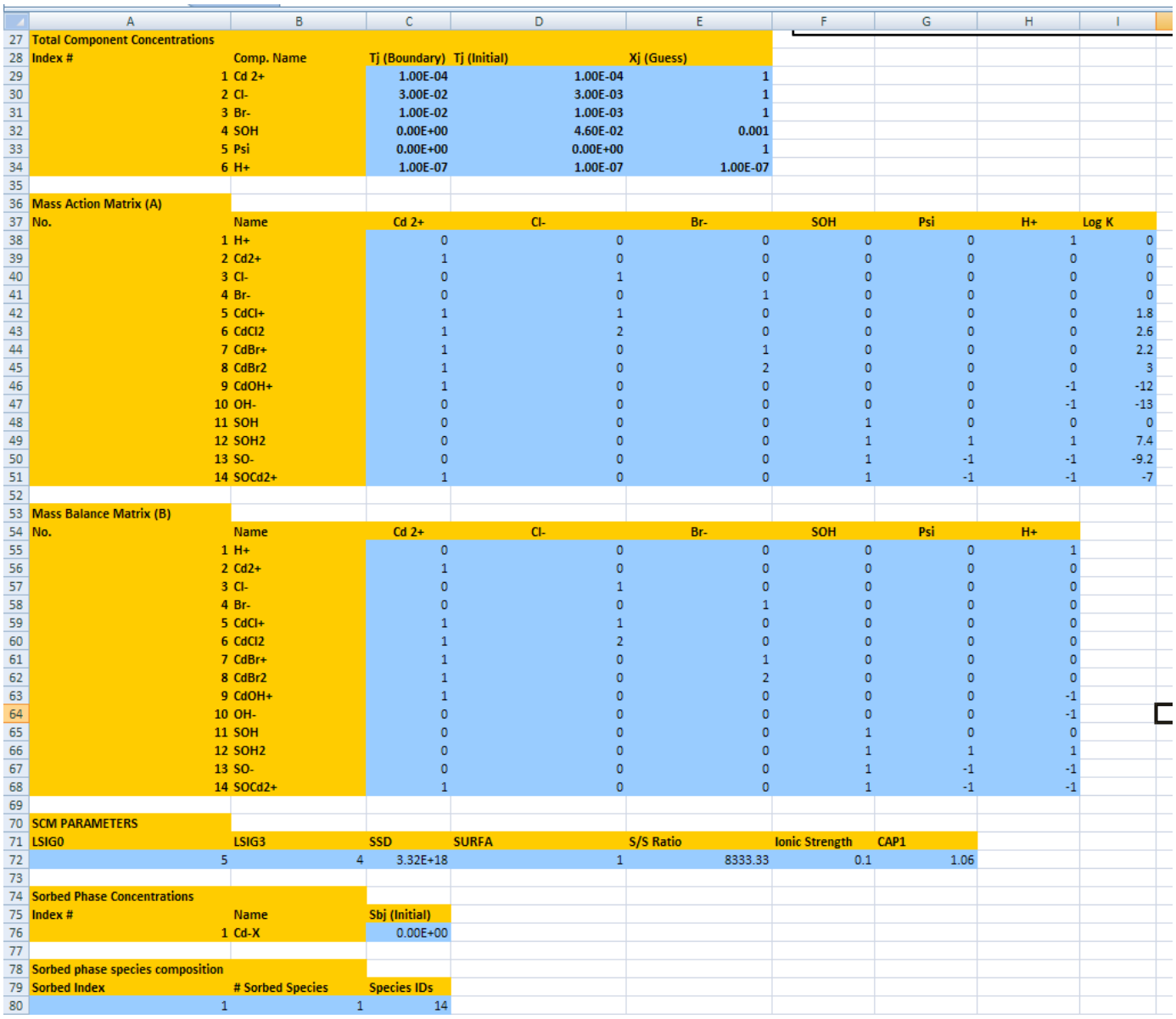
This is benchmark problem 4 for Torlapati and Clement (2012). Cederberg *et al.* (1985) developed a mass transport model, TRANQL, for multicomponent solution system. They presented a finite element solution for cadmium, chloride and bromide transport in a one-dimensional column where complexation and sorption were considered. The reaction involves formation of aqueous and surfaces complexes and sorption of free cadmium described by constant capacitance model.

1. For this problem, we need to set up the parameters in the geochemistry type problem. The simulation option will be 4 because this problem couples transport with geochemistry equilibrium.
2. Input the advection-dispersion parameters for this problem as shown in Figure 40 and set the number of components, species, aqueous components of interest and the sorbed components that are required to correct the concentrations of the aqueous components. The pH is fixed at 7 for this problem and hence the number of fixed component concentrations for this example problem is 1.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	10	m	
4		Total Time	15	day	
5		Pulse Time	15	day	
6		delx	0.03	m	
7		delt	0.06	day	
8		Velocity	0.333	m/day	
9		Dispersion coefficient	0.00666	m2/day	
10		Adv-Disp Type	2		
11		Problem Type (PT)	4		
12					
13					
14					
15	Kinetics Type Problem (PT = 1 & 2)			Geochemistry Type Problem (PT = 3 & 4)	
16	# Mobile Components	N/A		# Components	6
17	# Immobile Components	N/A		# Species	14
18	RXN Package #	N/A		# Fixed Comp Concentrations	1
19	ODE Solver Type	N/A		# Aqueous Concentrations	3
20	Reaction Terms	N/A		# Sorbed Concentrations	1
21				SCM TYPE	1

Figure 40. Advection-dispersion parameters for example problem-8

3. There are 3 aqueous components of interest of the total 6 components. These are Cd2+, Br- and Cl- and one sorbed species (a complex of cadmium formed by surface complexation) that is used to correct the concentration of Cd2+ to allow it to be transported along the column.
4. The SCM type for this model is constant capacitance. The short code for this type of surface complexation model in MICROQL is 1.
5. Press the "generate input template" button to enter the tableau (mass action and mass balance) as shown in Figure 41. For this problem both mass action and mass balance matrices are same.
6. Refer to the Figure 41 for the initial and boundary conditions and the surface complexation parameters for this problem.
7. The final table refers to the composition of the sorbed concentration. In this case, the sorbed concentration is only composed one surface complex of cadmium (species 14 – SoCd2+)
8. The results for this simulation are shown in Figure 42.
9. Please refer to the "Input guide" provided with the RT1D package or Torlapati and Clement (2012) to obtain the parameters in case the Figure 41 is unclear.



	A	B	C	D	E	F	G	H	I
27	Total Component Concentrations								
28	Index #	Comp. Name	Tj (Boundary)	Tj (Initial)	Xj (Guess)				
29	1	Cd 2+	1.00E-04	1.00E-04	1				
30	2	Cl-	3.00E-02	3.00E-03	1				
31	3	Br-	1.00E-02	1.00E-03	1				
32	4	SOH	0.00E+00	4.60E-02	0.001				
33	5	Psi	0.00E+00	0.00E+00	1				
34	6	H+	1.00E-07	1.00E-07	1.00E-07				
35									
36	Mass Action Matrix (A)								
37	No.	Name	Cd 2+	Cl-	Br-	SOH	Psi	H+	Log K
38	1	H+	0	0	0	0	0	1	0
39	2	Cd2+	1	0	0	0	0	0	0
40	3	Cl-	0	1	0	0	0	0	0
41	4	Br-	0	0	1	0	0	0	0
42	5	CdCl+	1	1	0	0	0	0	1.8
43	6	CdCl2	1	2	0	0	0	0	2.6
44	7	CdBr+	1	0	1	0	0	0	2.2
45	8	CdBr2	1	0	2	0	0	0	3
46	9	CdOH+	1	0	0	0	0	-1	-12
47	10	OH-	0	0	0	0	0	-1	-13
48	11	SOH	0	0	0	1	0	0	0
49	12	SOH2	0	0	0	1	1	1	7.4
50	13	SO-	0	0	0	1	-1	-1	-9.2
51	14	SOCd2+	1	0	0	1	-1	-1	-7
52									
53	Mass Balance Matrix (B)								
54	No.	Name	Cd 2+	Cl-	Br-	SOH	Psi	H+	
55	1	H+	0	0	0	0	0	1	
56	2	Cd2+	1	0	0	0	0	0	
57	3	Cl-	0	1	0	0	0	0	
58	4	Br-	0	0	1	0	0	0	
59	5	CdCl+	1	1	0	0	0	0	
60	6	CdCl2	1	2	0	0	0	0	
61	7	CdBr+	1	0	1	0	0	0	
62	8	CdBr2	1	0	2	0	0	0	
63	9	CdOH+	1	0	0	0	0	-1	
64	10	OH-	0	0	0	0	0	-1	
65	11	SOH	0	0	0	1	0	0	
66	12	SOH2	0	0	0	1	1	1	
67	13	SO-	0	0	0	1	-1	-1	
68	14	SOCd2+	1	0	0	1	-1	-1	
69									
70	SCM PARAMETERS								
71	LSIG0	LSIG3	SSD	SURFA	S/S Ratio	Ionic Strength	CAP1		
72	5	4	3.32E+18	1	8333.33	0.1	1.06		
73									
74	Sorbed Phase Concentrations								
75	Index #	Name	Sbj (Initial)						
76	1	Cd-X	0.00E+00						
77									
78	Sorbed phase species composition								
79	Sorbed Index	# Sorbed Species	Species IDs						
80	1	1	14						

Figure 41. Geochemistry input details for example problem – 8

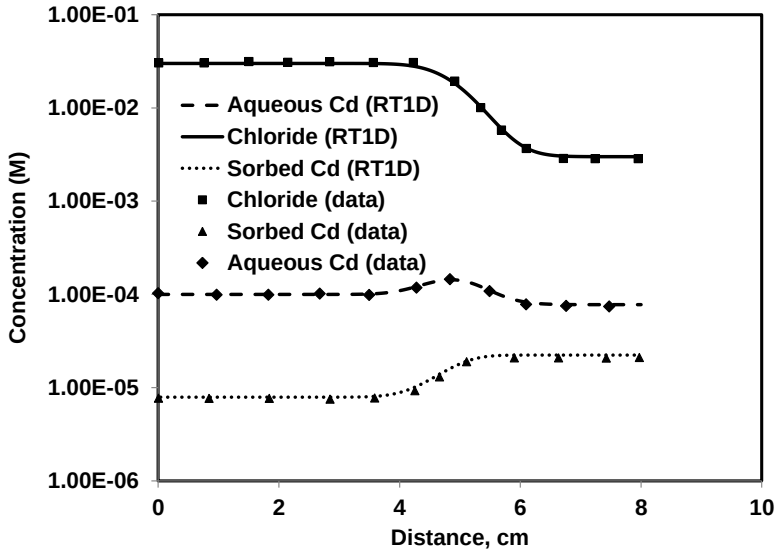


Figure 42. RT1D simulation results for the example problem 8

4.9 EXAMPLE-9: SEQUENTIAL BATCH REACTOR

This is the benchmark problem in Torlapati and Clement (2012). We simulate a sequential batch reactor set-up using the transport coupled with adsorption of arsenic described by the surface complexation.

1. There are a total of 3 sequential batch reactors for this problem and we will consider an equivalent 3cm length column with 4 nodes where one extra node is designated as the boundary node to supply the concentration to the other nodes.
2. We will consider 1cm/day velocity and dispersion effects are ignored. We will grid size of 1cm and time step of 1 day to ensure that the courant number is 1.
3. We will use explicit advection scheme (shortcode 0) to simulate one node advection with courant number 1. Set the transport parameters as shown in Figure 43.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	3	m	
4		Total Time	18	day	
5		Pulse Time	14	day	
6		delx	1	m	
7		delt	1	day	
8		Velocity	1	m/day	
9		Dispersion coefficient	0	m2/day	
10		Adv-Disp Type	0		
11		Simulation Option (SO)	4		
12					
13					
14					
15		Kinetics Type Problem (SO = 1 & 2)		Geochemistry Type Problem (SO = 3 & 4)	
16		# Mobile Components	N/A	# Components	4
17		# Immobile Components	N/A	# Species	12
18		RXN Package #	N/A	# Fixed Comp Concentrations	1
19		ODE Solver Type	N/A	# Aqueous Concentrations	1
20		# Reaction Parameters	N/A	# Sorbed Concentrations	1
21				SCM TYPE	2

Figure 43. Transport parameters for the example problem 9

4. The adsorption of arsenic is described by diffuse dual layer model (short code – 2)
5. The tableau, initial and boundary conditions can be set using the Figure 44. The sorbed arsenic concentration is composed of 3 species (8, 9, and 10).
6. The results for this simulation are shown in Figure 45.

	A	B	C	D	E	F	G	H
27	Total Component Concentrations							
28	Index #	Comp. Name	Tj (Boundary)	Tj (Initial)	Xj (Guess)			
29	1	AsO4[-3]	1.25E-06	0.00E+00	1.00E-03			
30	2	SOH	0.00E+00	0.00E+00	1.00E-03			
31	3	Psi	0.00E+00	0.00E+00	1.00E-03			
32	4	H+	1.00E-07	1.00E-07	1.00E-07			
33								
34	Mass Action Matrix (A)							
35	No.	Name	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Log K	
36	1	H+	0	0	0	1	0	
37	2	AsO4[-3]Aq	1	0	0	0	0	
38	3	FeOH	0	1	0	0	0	
39	4	OH-	0	0	0	-1	-13.91	
40	5	HAsO4[-2]	1	0	0	1	11.23	
41	6	H2AsO4[-1]	1	0	0	2	18.01	
42	7	H3AsO4	1	0	0	3	20.16	
43	8	>FeH2AsO4	1	1	0	3	31.44	
44	9	>FeHAsO4-	1	1	-1	2	26.18	
45	10	>FeAsO4-2	1	1	-2	1	20.1	
46	11	>FeOH2[+]	0	1	1	1	7.17	
47	12	>FeO[-]	0	1	-1	-1	-9.32	
48								
49	Mass Balance Matrix (B)							
50	No.	Name	Comp. 1	Comp. 2	Comp. 3	Comp. 4		
51	1	Species 1	0	0	0	1		
52	2	Species 2	1	0	0	0		
53	3	Species 3	0	1	0	0		
54	4	Species 4	0	0	0	-1		
55	5	Species 5	1	0	0	1		
56	6	Species 6	1	0	0	2		
57	7	Species 7	1	0	0	3		
58	8	Species 8	1	1	0	3		
59	9	Species 9	1	1	-1	2		
60	10	Species 10	1	1	-2	1		
61	11	Species 11	0	1	1	1		
62	12	Species 12	0	1	-1	-1		
63								
64	SCM PARAMETERS							
65	LSIG0	LSIG3	LSIG1	SSDS	SSDW	SURFA	S/S Ratio	Ionic Strength
66	3	2	1	1.04E+18	1.04E+18	1.08	1	0.01
67								
68	Sorbed Phase Concentrations							
69	Index #	Name	Sbj (Initial)					
70	1	As-X	0					
71								
72	Sorbed phase species composition							
73	Sorbed Index	# Sorbed Species	Species IDs					
74	1	3	8	9	10			

Figure 44. Geochemistry parameters for example problem 9

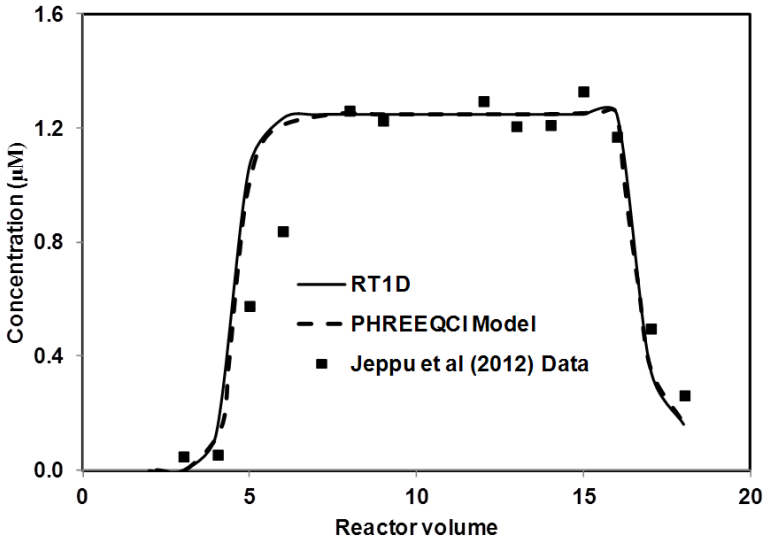


Figure 45. RT1D results for example problem 9

4.10 EXAMPLE-10: ION-EXCHANGE

Valocchi and Werth (2004) presented an analytical framework that allowed the characterization of certain key concentration profiles during the transport of ion-exchange solutes based on the chromatography theory. The validity of this theory was tested by applying it to a field situation in Palo Alto Baylands in California. The field project involved the injection of advanced municipal effluent into the aquifer. The principal chemical mechanism involved is the heterovalent ion exchange of Na+, Mg2+ and Ca2+.

1. Input the advection-dispersion and the geochemistry parameters as shown in Figure 46.

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	16	cm	
4		Total Time	5000	day	
5		Pulse Time	5000	day	
6		delx	1	cm	
7		delt	1	day	
8		Velocity	1.01	cm/day	
9		Dispersion coefficient	1	cm2/day	
10		Adv-Disp Type	1		
11		Simulation Option (SO)	4		
12					
13					
14					
15		Kinetics Type Problem (SO = 1 & 2)		Geochemistry Type Problem (SO = 3 & 4)	
16		# Mobile Components	N/A	# Components	5
17		# Immobile Components	N/A	# Species	7
18		RXN Package #	N/A	# Fixed Comp Concentrations	0
19		ODE Solver Type	N/A	# Aqueous Concentrations	3
20		# Reaction Parameters	N/A	# Sorbed Concentrations	3
21				SCM TYPE	0

Figure 46. Transport parameters for example problem 10

2. There is no surface complexation in this model and the adsorption occurs by ion exchange, so we set the SCM type to 0.
3. The initial, boundary, guess concentrations for the components and the tableau are given in Figure 47.

Total Component Concentrations								
Index #		Comp. Name	Tj (Boundary)	Tj (Initial)	Xj (Guess)			
	1	Na+	9.40E-03	2.48E-01	2.48E-01			
	2	Mg2+	4.94E-04	1.59E-01	1.59E-01			
	3	Ca2+	2.12E-03	1.65E-01	1.65E-01			
	4	X	7.50E-01	7.50E-01	7.50E-01			
	5	H+	0.00E+00	0.00E+00	1.00E-01			
Mass Action Matrix (A)								
No.		Name	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Log K
	1	Na+	1	0	0	0	0	0
	2	Mg2+	0	1	0	0	0	0
	3	Ca2+	0	0	1	0	0	0
	4	Na-X	1	0	0	1	-1	0
	5	Mg-X	0	1	0	2	-2	0.355
	6	Ca-X	0	0	1	2	-2	0.602
	7	H+	0	0	0	0	1	0
Mass Balance Matrix (B)								
No.		Name	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	
	1	Na+	1	0	0	0	0	
	2	Mg2+	0	1	0	0	0	
	3	Ca2+	0	0	1	0	0	
	4	Na-X	1	0	0	1	-1	
	5	Mg-X	0	1	0	2	-2	
	6	Ca-X	0	0	1	2	-2	
	7	H+	0	0	0	0	1	
Sorbed Phase Concentrations								
Index #		Name	Sbj (Initial)					
	1	Na-X	1.61E-01					
	2	Mg-X	1.41E-01					
	3	Ca-X	1.54E-01					
Sorbed phase species composition								
Sorbed Index		# Sorbed Species	Species IDs					
	1	1	4					
	2	1	5					
	3	1	6					

Figure 47. Geochemistry parameters for example problem 10

4. The sorbed species Na-X, Mg-X and Ca-X are composed of species 4, 5 and 6 respectively. These sorbed concentrations are used to correct the aqueous concentrations of Na+, Mg2+ and Ca2+ components respectively.
5. The results from these simulations are shown in Figure 48 a, b and c.

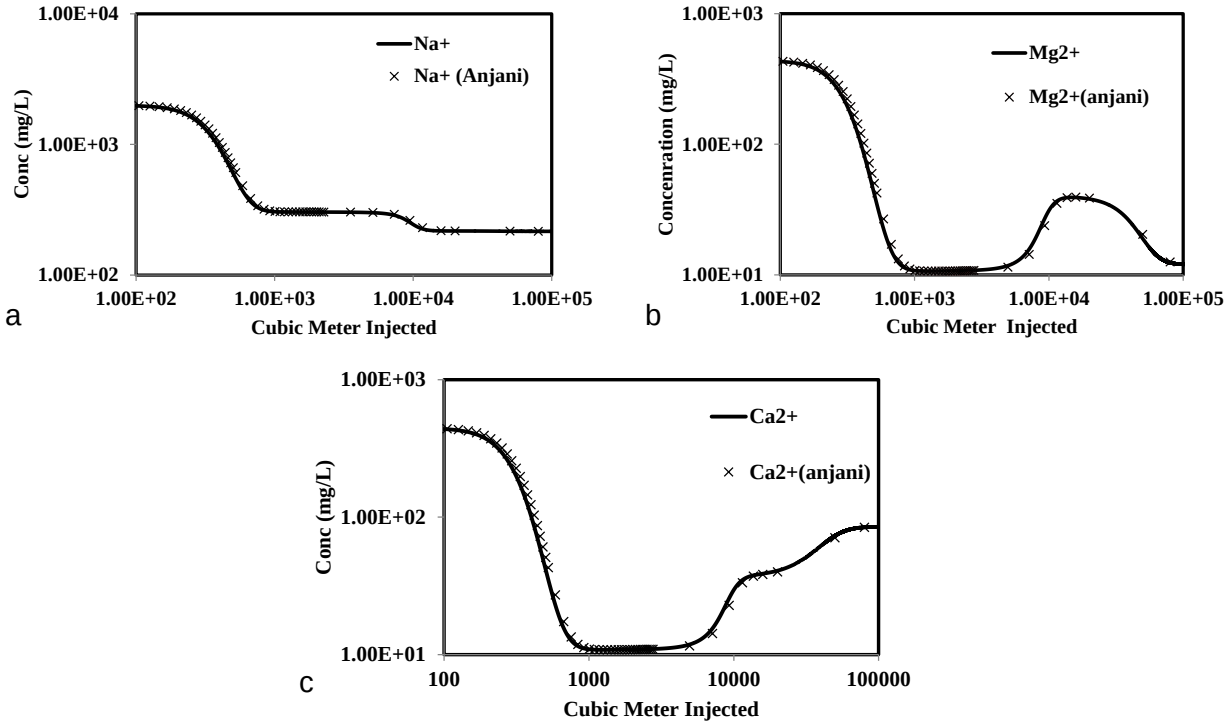


Figure 48. Results for example problem 10 a) Breakthrough profile for Na+ b) Breakthrough profile for Mg2+ c) Breakthrough profile for Ca2+

4.11 EXAMPLE-11: ARSENIC ADSORPTION ISOTHERM

In this example problem, we will consider the As(V) adsorption on to the goethite coated sand as shown in Jeppu *et al.* (2012). We will run RT1D with simulation option 3 to generate isotherm data. In this exercise, we will generate the isotherm data as if an experiment were being conducted. We will input the initial aqueous As(V) concentration in the solution and the program will give the adsorbed concentration and the equilibrium aqueous As(V) concentration. This can be done for different concentrations of As(V) and can be used to generate the isotherm data. The equilibrium equations for setting up the problem can be found in Jeppu *et al.* (2012).

1. Set up the input sheet as shown in Figure 49. This is a batch geochemistry problem so the simulation option must be set to 3 and all the transport parameters can be ignored. There are 4 components and 12 species in this example problem.
2. We are generating isotherms so there is only one aqueous species of interest i.e., the aqueous concentration of As(V). There are 3 sorbed complexes of As(V) that must be kept track of to calculate the equilibrium aqueous concentration. So we will set the number of sorbed concentrations to 3.
3. The pH is fixed for this problem and hence the number of fixed component concentrations is 1. Now we're ready to generate the input template sheet.
4. Input the geochemistry tableau, the initial aqueous concentration of arsenic and the surface complexation parameters as shown in Figure 50.

5. The 3 sorbed species of As(V) are 8, 9 and 10 in the species tableau. These will allow the program to calculate the sorbed concentration of As(V) and the equilibrium As(V) concentration in moles/L. The program sums up the concentrations of species 8, 9 and 10 to get the sorbed species concentration and subtracts this from the total aqueous concentration of As(V) to get the aqueous concentration of As(V).
6. The concentration of each species is presented in Table 3. The program also calculates the total aqueous and sorbed concentrations of As(V) in moles/L. This process can be repeated for different values of initial As(V) concentration and the generated data can be plotted go obtain isotherms.
7. The values of sorbed and aqueous arsenic concentration were consistent with the values observed in the paper and the comparison between the published data and the RT1D models simulations are presented in Figure 51.

F34

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	1	cm	
4		Total Time	1	day	
5		Pulse Time	1	day	
6		delx	1	cm	
7		delt	1	day	
8		Velocity	1	cm/day	
9		Dispersion coefficient	1	cm2/day	
10		Adv-Disp Type	1		
11		Simulation Option (SO)	3		
12					
13					
14					
15		Kinetics Type Problem (SO = 1 & 2)		Geochemistry Type Problem (SO = 3 & 4)	
16		# Mobile Components	N/A	# Components	4
17		# Immobile Components	N/A	# Species	12
18		RXN Package #	N/A	# Fixed Comp Concentrations	1
19		ODE Solver Type	N/A	# Aqueous Concentrations	1
20		# Reaction Parameters	N/A	# Sorbed Concentrations	3
21				SCM TYPE	2

Figure 49. Parameters for generating the input template in example problem 11

Species Name	Conc,i	
H+	1.11E-10	
AsO4[-3]Aq	2.75E-06	
FeOH	3.43E-05	
OH-	1.11E-04	
HAsO4[-2]	5.17E-05	
H2AsO4[-1]	3.46E-08	
H3AsO4	5.43E-16	
>FeH2AsO4	3.55E-09	
>FeHAsO4-	6.81E-07	
>FeAsO4-2	1.98E-05	

>FeOH2[+]	1.46E-05	
>FeO[-]	5.74E-07	
Comp. Name	Total Conc.	LogX(i)
AsO4[-3]	0.0000750000	-5.561436606
SOH	0.0000699435	-4.46412398
Psi	-0.0000262812	2.411678544
H+	0.0000000001	-9.954677021
Aq. Conc (moles/L)	Sorbed Conc (moles/L)	
5.453E-05	0.0000204731	

Table 3. Results from RT1D simulations for example problem 11

	A	B	C	D	E	F	G	H
28	Index #	Comp. Name	Total Conc(Ti)	Guess Conc(Xi)				
29	1	AsO4[-3]	7.50E-05	1.00E-05				
30	2	SOH	0.00E+00	1.00E-03				
31	3	Psi	0.00E+00	1.00E-03				
32	4	H+	1.11E-10	1.11E-10				
33								
34	Mass Action Matrix (A)							
35	Index #	Name	Comp 1	Comp 2	Comp 3	Comp 4	Log K	
36	1	H+	0	0	0	1	0	
37	2	AsO4[-3]Aq	1	0	0	0	0	
38	3	FeOH	0	1	0	0	0	
39	4	OH-	0	0	0	-1	-13.91	
40	5	HAsO4[-2]	1	0	0	1	11.23	
41	6	H2AsO4[-1]	1	0	0	2	18.01	
42	7	H3AsO4	1	0	0	3	20.16	
43	8	>FeH2AsO4	1	1	0	3	31.44	
44	9	>FeHAsO4-	1	1	-1	2	26.18	
45	10	>FeAsO4-2	1	1	-2	1	20.1	
46	11	>FeOH2[+]	0	1	1	1	7.17	
47	12	>FeO[-]	0	1	-1	-1	-9.32	
48								
49	Mass Balance Matrix (B)							
50	Index #	Name	Comp 1	Comp 2	Comp 3	Comp 4		
51	1	H+	0	0	0	1		
52	2	AsO4[-3]Aq	1	0	0	0		
53	3	FeOH	0	1	0	0		
54	4	OH-	0	0	0	-1		
55	5	HAsO4[-2]	1	0	0	1		
56	6	H2AsO4[-1]	1	0	0	2		
57	7	H3AsO4	1	0	0	3		
58	8	>FeH2AsO4	1	1	0	3		
59	9	>FeHAsO4-	1	1	-1	2		
60	10	>FeAsO4-2	1	1	-2	1		
61	11	>FeOH2[+]	0	1	1	1		
62	12	>FeO[-]	0	1	-1	-1		
63								
64	SCM PARAMETERS							
65	LSIG0	LSIG3	LSIG1	SSDS	SSDW	SURFA	S/S Ratio	Ionic Strength
66	3	2	1	1.56E+18	1.56E+18	54	0.5	0.01
67								
68	Sorbed Species ID #							
69	Index #	Species Name	Species #					
70	1	Sorbed Sp 1	8					
71	2	Sorbed Sp 2	9					
72	3	Sorbed Sp 3	10					
73								
74	Component # of Aq species	1						

Figure 50. Geochemistry parameters for example problem 11

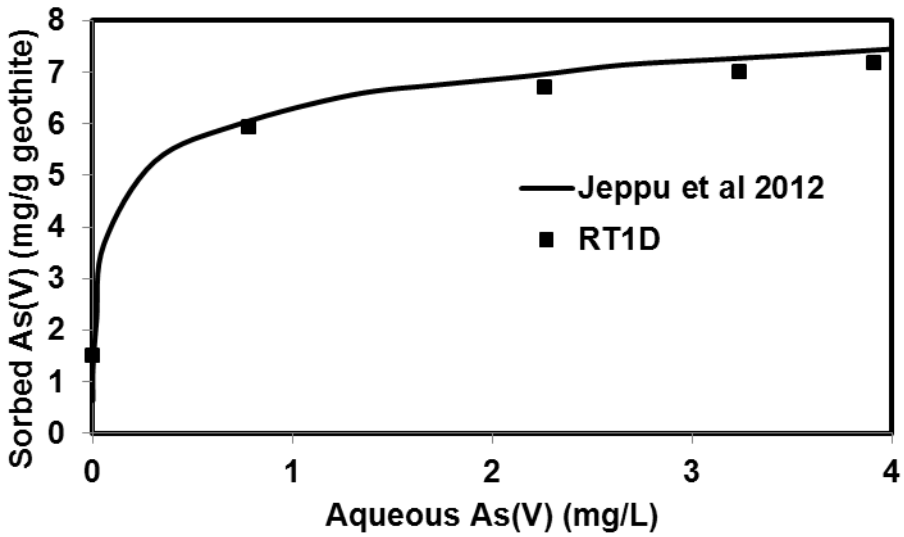


Figure 51. As(V) adsorption curve for pH=7

4.12 EXAMPLE-12: CALCIUM CARBONATE SPECIATION

In this test problem, we will consider the speciation of a solution to which 10^{-3} moles/L of $CaCO_3$ has been added, when it reaches equilibrium.

1. Set up the spreadsheet as shown in Figure 52. The program ignores all the advection-dispersion parameters when simulation option 3 is chosen as explained earlier.

A64

	A	B	C	D	E
1		Advection-Dispersion Parameters			
2		Parameter Name	Value	Units	
3		Length	1	cm	
4		Total Time	1	day	
5		Pulse Time	1	day	
6		delx	1	cm	
7		delt	1	day	
8		Velocity	1	cm/day	
9		Dispersion coefficient	1	cm2/day	
10		Adv-Disp Type	1		
11		Simulation Option (SO)	3		
12					
13					
14					
15	Kinetics Type Problem (SO = 1 & 2)			Geochemistry Type Problem (SO = 3 & 4)	
16	# Mobile Components	N/A		# Components	3
17	# Immobile Components	N/A		# Species	9
18	RXN Package #	N/A		# Fixed Comp Concentrations	0
19	ODE Solver Type	N/A		# Aqueous Concentrations	1
20	# Reaction Parameters	N/A		# Sorbed Concentrations	1
21				SCM TYPE	0

Figure 52. Parameters to generate the input template sheet for example problem 12

2. Input the tableau, the total and guess concentration for each component as shown in Figure 53.
3. Since we are not generating isotherms, enter 0 for both "Component of Aqueous species" and "Sorbed species ID". This tells the program not to calculate the aqueous phase and solid phase concentrations.
4. The speciation for this example problem is presented in Table 4

Species Name	**Conc,i**	
Ca2+	6.87E-04	
CaOH+	1.12E-05	
CaHCO3+	4.58E-06	
CaCO3(aq)	2.97E-04	
H2CO3*	2.05E-08	
HCO3-	2.65E-04	
CO32-	4.33E-04	
H+	3.87E-11	
OH-	2.59E-04	
Comp. Name	**Total Conc.**	**LogX(i)**
Ca2+	0.001	-3.163110315
CO32-	0.001	**-3.363665504**
H+	0	-10.41270197

Table 4. RT1D simulation results for example problem 12

27	Total Component Concentrations						
28	Index #	Comp. Name	Total Conc(Ti)	Guess Conc(Xi)			
29	1	Ca2-	1.00E-03	1.00E-03			
30	2	CO32-	1.00E-03	1.00E-06			
31	3	H+	0.00E+00	1.00E-09			
32							
33	Mass Action Matrix (A)						
34	Index #	Name	Comp 1	Comp 2	Comp 3	Log K	
35	1	Ca2-	1	0	0	0	
36	2	CaOH-	1	0	-1	-12.2	
37	3	CaHCO3-	1	1	1	11.6	
38	4	CaCO3(aq)	1	1	0	3	
39	5	H2CO3*	0	1	2	16.5	
40	6	HCO3-	0	1	1	10.2	
41	7	CO32-	0	1	0	0	
42	8	H-	0	0	1	0	
43	9	OH-	0	0	-1	-14	
44							
45	Mass Balance Matrix (B)						
46	Index #	Name	Comp 1	Comp 2	Comp 3		
47	1	Ca2-	1	0	0		
48	2	CaOH-	1	0	-1		
49	3	CaHCO3-	1	1	1		
50	4	CaCO3(aq)	1	1	0		
51	5	H2CO3*	0	1	2		
52	6	HCO3-	0	1	1		
53	7	CO32-	0	1	0		
54	8	H-	0	0	1		
55	9	OH-	0	0	-1		
56							
57	Sorbed Species ID #						
58	Index #	Species Name	Species #				
59	1	Sorbed Sp 1	0				
60							
61	Component # of Aq species	0					

Figure 53. Geochemistry parameters for example problem 12

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